THE STUDY OF ELECTRON CORRELATION

by

" DIFFERENT ORBITALS FOR DIFFERENT SPINS" METHODS.

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Hirst,D.M. and Linington,M.E., Theoret. chim. Acta,(Berl.), 22,(1971),315.
"The method of non-paired spatial orbitals - Naphthalene and Azulene."

Hirst,D.M. and Linington,M.E., Theoret. chim. Acta,(Berl.), 26,(1972),176.
"The method of non-paired spatial orbitals - part II, the Benzyl radical."

Hirst,D.M. and Linington,M.E.,J. Chem. Soc.,(London), Farad. Trans. II, 68,(1972),1988.
"The method of non-paired spatial orbitals - part III, Anthracene and Phenanthrene."

Hirst,D.M. and Linington,M.E., J. Chem. Soc.,(London), Farad.Trans. II, 68,(1972),2200.
"The method of non-paired spatial orbitals - part IV, Density matrix methods for calculating wavefunctions with full spin projection."

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ABSTRACT.

The bulk of this thesis is concerned with the calculation of molecular wavefunctions - calculated within a Different Orbitals for Different Spins framework.

Initially other important methods of constructing molecular wavefunctions are considered, and the DODS method is discussed in relation to them. Two different DODS methods are considered in detail, namely the Alternant Molecular Orbital method and the Non-Paired Spatial Orbital method.Other workers have previously used these methods and obtained satisfactory wavefunctions. Both methods make good allowance for electron correlation, but for benzene, and several other hydrocarbons, the NPSO method proves superior. Pauncz has stated that,(67), because the NPSO calculations are cumbersome,"one cannot expect to apply this method to larger systems." In this thesis ths NPSO method is extended to larger molecules, namely azulene, anthracene and phenanthrene. In all cases the NPSO method proves superior to the AMO method. With azulene, for example,a better ground state energy is obtained using a one-parameter NPSO wavefunction, than with a five-parameter optimised AMO wavefunction.

Having found satisfactory ground state wavefunctions for these molecules, and observed that most endorse the suggestion that $k_{min} \simeq 0.25$, the NPSO method was applied to open shell systems, such as benzyl radical, and butadiene negative ion. The results for the benzyl

radical are more satisfactory than for other open shell systems. The spin density distribution of the benzyl radical was calculated by various approximations, but with limited success. In this context we developed a fully spin projected NPSO method.

I. INTRODUCTION

I.I: Solution of the Schrödinger Wave Equation.

The study of the electronic structure of molecules is based on the search for a solution of the Schrödinger wave equation (1), since the electronic structure and properties any molecule can be derived from the wave function.

$$H\psi = E\psi \qquad \text{..I-1}$$

where, for n electrons, the Hamiltonian operator is

$$H = \sum_{i=1}^{n} \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{a} \frac{Z_a e^2}{r_{ia}} \right) + \sum_{i<j}^{n} \frac{e^2}{r_{ij}} \qquad \text{..I-2}$$

This form of the Hamiltonian already assumes that:-

1) only stationary states are being considered;

2) spin-orbit interactions are neglected; and

3) the Born-Oppenheimer approximation (2) holds.

The expectation value of the Hamiltonian operator, $\langle H \rangle$, is given by

$$\langle H \rangle = \int \psi^* H \psi \, \delta\tau \Big/ \int \psi^* \psi \, \delta\tau \qquad \text{..I-3}$$

and is regarded as the total electronic energy, E.

For a many electron system, the exact solution of the equation (I-1) is not possible, but there are useful approximate methods. Hartree (3) assumed that each electron moves independantly of, but under an average potential due to the other electrons, in an orbital $\psi_i(x_i)$, x_i denotes electron position. This "Independant Particle Model" (4) assumes that the wavefunction is a simple product

of one electron orbitals

$$\underline{\Psi} = \psi_1(1)\ \psi_2(2)\ \psi_3(3) \ldots\ldots\ \psi_{n-1}(n-1)\ \psi_n(n) \qquad \text{..I-4}$$

This form of the wavefunction would be valid if there were no electron repulsion terms of the form $\frac{1}{r_{ij}}$ in H, but the Hartree method does include the average potential due to the other electrons.

The electronic energy, E, is now the sum of the energies of the individual electrons.

I.2: Electron correlation (5)

Since electron repulsion terms are neglected in the Hartree method, there is, in theory, a finite probability of two electrons having the same position co-ordinates. In fact there is no correlation between the motions of the individual electrons.

There are two types of electron correlation:-

a) Fermi Holes (6)

The Pauli Principle states (7) that all particles with half-integral spin are described by antisymmetric wavefunctic Since electrons have half-integral spin, they are in fact fermions; the result is the exclusion principle. No two electrons can have the same four quantum numbers: that is, no two electrons of the same spin can occupy the same part of space.

b) Coulomb Holes (8)

For electrons of the same spin there will be a Fermi hole; but for electrons of opposite spin there will be no Fermi hole. Thus there is a finite probability of two electrons occupying the same part of space. However there will be a charge interaction between two electrons of $-e^2/r_{ij}$, if they are a distance r_{ij} apart. As r_{ij} tends to zero, as the electrons approach each other, this interaction will become infinite. Thus it is not possible for two electrons to approach each other closer than a fixed distance, and a Coulomb hole results.

A Fermi hole is due to spin interactions, but a Coulomb hole is due to charge interactions. A Coulomb hole imposes the restriction that no two electrons, irrespective of spin, can occupy the same part of space.

I-3: Including correlation in the wavefunction.

a) Spin correlation.

The Hartree wavefunction, equation I-4, is unsatisfactory for two reasons: (i) it ignores the spins of the electrons, and (ii) it does not treat them as indistinguishable particles

The wavefunction can be written as a product of spin orbital ϕ_i, each consisting of a space orbital $\psi_i(x_i)$ and a spin factor $\alpha(x_i)$ or $\beta(x_i)$. Each space orbital can occur twice; once with a spin factor of $\alpha(x_i)$, and once with factor $\beta(x_i)$. Thus:-

$$\Psi = \psi_1(x_1)\alpha(x_1)\,\psi_1(x_2)\beta(x_2)\cdots\cdots\,\psi_{\frac{n}{2}}(x_{n-1})\alpha(x_{n-1})\,\psi_{\frac{n}{2}}(x_n)\beta \qquad \text{..I-5}$$

It is more convenient to define a set of spin orbitals,

$$\phi_i(i) = \psi_i(x_i)\,\alpha(x_i)$$

and

$$\overline{\phi_i}(i) = \psi_i(x_i)\,\beta(x_i) \qquad \text{..I-6}$$

and thus:-

$$\bar{\Psi} = \phi_1(1)\,\overline{\phi_1}(2)\,\ldots\,\phi_{\frac{n}{2}}(n-1)\,\overline{\phi_{\frac{n}{2}}}(n) \qquad \text{..I-7}$$

To make allowance for the indistinguishability of the electrons we must include all permutations of the electrons in the spin orbitals:

$$\bar{\Psi} = \sum_P a_P P\;\phi_1(1)\,\overline{\phi_1}(2)\,\ldots\,\phi_{\frac{n}{2}}(n-1)\,\overline{\phi_{\frac{n}{2}}}(n) \qquad \text{..I-8}$$

P denotes permutations,

and a_P is a numerical coefficient.

The Pauli principle requires that interchange of two electrons changes the sign of the wavefunction, giving

$$\bar{\Psi} = \sum_P (-1)^P P\;\phi_1(1)\,\overline{\phi_1}(2)\,\ldots\,\phi_{\frac{n}{2}}(n-1)\,\overline{\phi_{\frac{n}{2}}}(n) \qquad \text{..I-9}$$

where, for an odd number of interchanges $(-1)^P = -1$, and $+1$ for an even number.

This can be written as:-

$$\bar{\Psi} = A\,|\,\phi_1(1)\,\overline{\phi_1}(2)\,\ldots\,\phi_{\frac{n}{2}}(n-1)\,\overline{\phi_{\frac{n}{2}}}(n)\,| \qquad \text{..I-10}$$

where A is the antisymmetriser,

$$A = \sum_P (-1)^P P .$$

Equation I-9 is in fact the expansion of a determinant. Thus the wavefunction can be written in terms of a Slater determinant (9); all possible permutations of electrons are included, and since the determinant vanishes if any two rows or columns are the same, Fermi holes are included also.

b) Space correlation.

Although the Hartree- Fock (HF) method (10) takes into account spin correlation - through the use of a Slater determinant, it makes no allowance for space correlation. It finds the wavefunction for each electron in the presence of an average potential due to the remaining electrons, and hence it neglects the "instantaneous" repulsions between pairs of electrons. There will thus be a difference between the energy calculated from the exact solution of the Schrödinger wave equation, and the HF energy. This difference is known as the correlation energy (23).

I.4: Methods of including space correlation in the wavefunction.

Several methods (14,13,12) have been developed to try to include some space correlation in the wavefunction.

(i)Correlated Wavefunction. (11)

One possible method of introducing a coulomb hole into the wavefunction is to include the interelectronic distance, r_{ij}, explicitly. Hylleraas (14), James and Coolidge (15) developed this method. It works well for two electron systems, such as Helium or Hydrogen, but its application to systems with larger numbers of electrons is difficult, because the

mathematics becomes unmanagable. The problem is the evaluati of the expectation value of the Hamiltonian, when the integrals involved contain more than one interelectronic distance. Szász (16) has recently performed more calculation in an effort to extend the range of applicability of this method.

Sinanoğlu (12) proposed another method of incorporating r_{ij} into the wavefunction - the many electron theory. He showed that, in HF theory, the long range potentials are taken into account. Having expressed the wavefunction in terms of the HF wavefunction, and a correction term, he expanded the correction term as two, three, four,.... electr excitations. Since the potentials neglected by HF theory, short range potentials, are due to the spin pairing of the electrons, he neglected all but the two electron terms in the expansion and so reduced the correction to a soluble two electron problem.

(ii) Configuration Interaction. (17)

The configuration interaction (CI) method - or superpositio of configurations method - was first considered by Hylleraas (18). A better approximation to the ground state wavefunction can be formed by allowing for interactions between the HF ground state, ψ_0 , and the excited state configurations. Since every normalisable antisymmetric wavefunction can be expressed as a linear combination of Slater determinants built up from a complete basis set of one electron functions (19) we can expand the total wavefunction as

$$\psi_T = \sum_{k=0} C_k \psi_k \qquad \text{..I-11}$$

The coefficients, C_k, that will give the best solution to equation I-1 can be found by the variation principle (20). A set of linear equations is formed,

$$\sum_k (H_{kl} - E S_{kl}) C_l = 0 \qquad \text{..I-12}$$

which may be solved if

$$\det [H_{kl} - E S_{kl}] = 0 \qquad \text{..I-13}$$

where

$$H_{kl} = \int \psi_k H \psi_l \, d\tau, \quad S_{kl} = \int \psi_k \psi_l \, d\tau.$$

The theory of the method is simple; the practical application is frought with difficulties. Using a complete basis set means the size of the secular determinant is huge. Despite the reduction in the number of configurations that need to be included, through considering spin and symmetry restrictions, the task is still mammoth. To worsen the situation, convergence is slow. By varying the basis orbitals at the same time as varying the coefficients we can improve the situation. This is multiconfigurational Self-consistent Field (SCF) CI. (21)

(iii) Different Orbitals for Different Spins, DODS. (22)

We have already noted, that, for closed shell systems, the same space orbital is used twice, in a determinantal wavefunction. Since some electron correlation is due to the interactions between electrons in these doubly occupied orbitals, a better wavefunction could be formed by putting electrons of different spin into different space orbitals.

Thus:-

$$\Psi = |\, \psi_1(1)\alpha(1)\ \ \psi_2(2)\alpha(2)\ \ \ldots\ \ \psi_n(n)\alpha(n)\ \ \psi_{n+1}(n+1)\beta(n+1)\ \ldots\ \ \psi_{2n}(2n)\beta(2n)\,| \qquad \text{..I-14}$$

The bulk of this thesis will be devoted to the calculation of molecular wavefunctions and properties using DODS methods.

II. HARTREE-FOCK THEORY.(10)

II.I:Introduction.

In order to find the best wavefunction, Ψ , of a particular form, the variation principle (25) is applied and the expectation value of the Hamiltonian, H, is minimised. This expectation value is the energy, E,

$$E = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} \quad . \qquad ..2\text{-}1$$

The energy can be calculated using an initial approximate wavefunction which can be varied with respect to the starting orbitals and the variation set equal to zero. Solving the resulting problem, by the method of Lagrangian multipliers(24), gives a set of coupled integro-differential equations. The solution of these coupled equations gives the best wavefunction consistent with the initial approximation.

If a simple product of one electron orbitals is used as the initial wavefunction the Hartree equations (3) are obtained. If a Slater determinant (9) is used the Hartree- Fock equations are formed,(10).

II.2: Hartree-Fock Equations.

For a determinantal wavefunction for a closed shell system

$$\Psi = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \cdots \quad \psi_{\frac{n}{2}} \bar{\psi}_{\frac{n}{2}}| \qquad ..2\text{-}2$$

the energy is given by

$$E = 2\sum_{i=1}^{n/2} I_{ii} + \sum_i \sum_j (2J_{ij} - K_{ij}) \qquad ..2\text{-}3$$

where:-

i)

$$I_{ii} = \int \psi_i^*(1)\, h_{core}(1)\, \psi_i(1)\, d\tau_1 \qquad ..2\text{-}4a$$

$h_{core}(1)$ is the one electron part of equation 1-2, the Hamiltonian, $\left[-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Z_A e^2}{r_{iA}}\right]$

ii)

$$J_{ij} = \iint \psi_i^*(1)\, \psi_i(1)\, \frac{1}{r_{12}}\, \psi_j^*(2)\, \psi_j(2)\, d\tau_1 d\tau_2 \qquad ..2\text{-}4b$$

is a coulomb integral, accounting for repulsions between the electrons in orbitals ψ_i and ψ_j ,

and

iii)

$$K_{ij} = \iint \psi_i^*(1)\, \psi_j(1)\, \frac{1}{r_{12}}\, \psi_i^*(2)\, \psi_j(2)\, d\tau_1 d\tau_2 \qquad ..2\text{-}4c$$

is an exchange integral.

From this the HF equations are obtained as, assuming real orbitals,

$$\left[h_{core}(1) + \sum_j (2J_j(1) - K_j(1)\right] \psi_i(1) = \epsilon_i \psi_i(1) \qquad ..2\text{-}5$$

where $J_j(1)$ and $K_j(1)$ are defined from

$$K_{ij} = \int \phi_i(1)\, K_j(1)\, \phi_i(1)\, d\tau_1 = \int \phi_j(2)\, K_i(2)\, \phi_j(2)\, d\tau_2 \qquad ..2\text{-}6a$$

and

$$J_{ij} = \int \phi_i(1)\, J_j(1)\, \phi_i(1)\, d\tau_1 = \int \phi_j(2)\, J_i(2)\, \phi_j(2)\, d\tau_2 \qquad ..2\text{-}6b$$

that is:

$$F\psi_i = \epsilon_i \psi_i \qquad ..2\text{-}7$$

In order to solve these equations an iterative procedure is used. The initial orbitals are guessed, used to calculate K_j and J_j, which are in turn used to solve equation 2-7 for a better approximate wavefunction. This procedure is repeated until there is no variation in either the orbitals or the energy; that is until self consistency results.

II.3:Hartree-Fock for Molecules,(26).

For atoms we can solve the HF equations. For molecules, because of the lack of spherical symmetry, the linear combination of atomic orbitals - LCAO - approximation should be used.

For closed shell molecules HF calculations are usually performed by the Roothaan method (24) in which the molecular wavefunctions ψ_i can be expanded in terms of the atomic orbitals χ_i, as

$$\psi_i = \sum_r C_{ir} \chi_r \qquad ..2\text{-}8$$

Substituting equation 2-8 into equation 1-1 and applying the variation principle results in an equation analogous to equation 2-7,

$$\sum_s F_{rs} C_{su} = \sum_s C_{su} \epsilon_u S_{rs} \qquad ..2\text{-}9$$

where $F_{rs} = \int \chi_r(1)\, h(1)\, \chi_s(1)\, d\tau +$

$$\sum_{tu} P_{tu}\left[2\iint \chi_r(1)\chi_t(1)\frac{1}{r_{12}}\chi_s(2)\chi_u(2)\, d\tau_1 d\tau_2 - \iint \chi_r(1)\chi_t(2)\frac{1}{r_{12}}\chi_u(1)\chi_s(2)\, d\tau_1 d\tau_2\right] \qquad ..2\text{-}10$$

P_{tu} is defined as the bond order matrix, (27).

$$P_{tu} = \sum_{m=1}^{n/2} C_{tm} C_{um} \qquad ..2\text{-}11$$

The energy, E, is given by

$$E = \frac{1}{2}\sum_{r}\sum_{s} P_{rs}\,(H_{rs} + F_{rs}) \qquad ..2\text{-}12$$

Again an iterative SCF method is used to solve the equations.

II.4:Hartree-Fock theory for Open Shell Systems, (28).

HF theory seeks the best single determinant wavefunction with doubly filled orbitals. However it can be extended to open shell systems; but firstly some of the spin properties of the wavefunction will be considered.

Spin properties of the wavefunction:

In writing the Hamiltonian operator as equation 1-2, spin-orbit coupling was ignored, thus H is spin free. In this case the Hamiltonian operator, (29,30), must commute with both the total spin operator, S^2, and the z-component, S_z .That is:

$$HS^2 = S^2H \qquad ..2\text{-}13$$

and

$$HS_z = S_z H, \qquad S^2 = S_z^2 + S_x^2 + S_y^2$$

Thus the wavefunction, ψ, an eigen-function of H, must also be an eigen-function of the operators S_z and S^2. Although the formation of a wavefunction, in terms of a product of one-electron orbitals, that is an eigen-function of S_z is easy, it is considerably more difficult to make such a wavefunction an eigen-function of S^2. A Slater determinant of the type so far considered (equation 1-7) will automatically be an eigen-function of both the S_z and S^2 operators, since it consists of doubly filled orbitals. For an open shell system the situation is different.

$$\psi = A\left|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_{\frac{n}{2}}\bar{\phi}_{\frac{n}{2}}\phi_{n+1}\phi_{n+2}\right| \qquad ..2\text{-}14$$

In general, if a determinantal wavefunction for an open shell system, (equation 2-14), has n_α, α spin electrons and n_β, β spin electrons, $n_\alpha \geq n_\beta$, it will not be an eigen-function of S^2 unless the number of doubly occupied orbitals is n_β, (30).

Open shell SCF Hartree-Fock theory:

Roothaan (28) and Huzinaga (31) extended SCF theory to open shell systems, such as radicals and excited states, using a wavefunction of the form of equation 2-14. Equation 2-9 still holds, but now the Fock operator, F_{rs}, is defined as:

$$F_{rs} = \langle \chi_r | (H + 2J_T - K_T) - (2\alpha J_o - \beta K_o) | \chi_s \rangle$$
$$+ P^{cc}_{tu} [S_{ru} B_{ts} + S_{ts} B_{ru}] + f P^{o}_{tu} [S_{ru} B_{ts} + S_{ts} B_{ru}]$$

..2-15

where

$$J_T = J_c + J_o = \sum_{k}^{\text{closed shells}} J_k + f \sum_{m}^{\text{open shells}} J_{m\,\text{open}}$$

$$K_T = K_c + K_o = \sum_{k}^{\text{closed shells}} K_k + f \sum_{m}^{\text{open shells}} K_m$$

$$\alpha = (1-a)/(1-f)$$

and $\beta = (1-b)/(1-f)$, a and b are numerical constants, depending on the system, (28).

f = fractional occupation number of open shells,

= number of occupied spin orbtials divided by the number of available spin orbitals.

$$B_{ru} = \langle \chi_r | 2\alpha J_o - \beta K_o | \chi_u \rangle$$

and

$$S_{ru} = \langle \chi_r | \chi_u \rangle .$$

and

$$P^{cc}_{tu} = \sum_{k}^{\text{closed shells}} C_{ku} C_{kt}$$

..2-16

and

$$P^{o}_{tu} = \sum^{\text{open shells}} C_{ku} C_{kt} \quad \text{and} \quad P^{T}_{tu} = P^{cc}_{tu} + P^{o}_{tu}$$

Here F_{rs} contains an open shell and a closed shell term. The energy is still given by equation 2-12.

Hartree-Fock theory extended to a DODS system,(32):

The unrestricted HF method (33) extends HF theory such that the initial wavefunction allows electrons of

different spins to occupy different spatial orbitals.

$$\underline{\Psi} = A\,|\phi_1(1)\alpha(1)\ \phi_2(2)\alpha(2)\ \cdots\ \phi_m(m)\alpha(m)\ \phi_{m+1}(m+1)\beta(m+1)\ \cdots\ \phi_n(n)\beta(n)\ | \quad ..2\text{-}17$$

The energy is now

$$E = \sum_i^n H_{ii} + \frac{1}{2}\sum_i^n\sum_j^n J_{ij} - \frac{1}{2}\left[\sum_i^m\sum_j^m K_{ij} + \sum_{i=m+1}^n\sum_{j=m+1}^n K_{ij}\right] \quad ..2\text{-}18$$

Applying the variation principle to this in the LCAO approximation leads to two pseudo-eigenvalue problems, for α and β electrons separately.

$$F^\alpha C_i^\alpha = \epsilon_i^\alpha S C_i^\alpha$$

$$F^\beta C_i^\beta = \epsilon_i^\beta S C_i^\beta \quad ..2\text{-}19$$

where

$$F^\alpha = H + J - K^\alpha \quad \text{and} \quad ..2\text{-}20$$

$$F^\beta = H + J - K^\beta$$

F_{rs}^α and F_{rs}^β are now defined as

$$F_{rs}^\alpha = H_{rs} + \sum_t\sum_u\left[(P_{tu}^\alpha + P_{tu}^\beta)\langle rs|tu\rangle - P_{tu}^\alpha\langle rs|ut\rangle\right] \quad ..2\text{-}21$$

$$F_{rs}^\beta = H_{rs} + \sum_t\sum_u\left[(P_{tu}^\alpha + P_{tu}^\beta)\langle rs|tu\rangle - P_{tu}^\beta\langle rs|ut\rangle\right]$$

$$\langle rs|tu\rangle = \int\chi_r(1)\,\chi_s(2)\,\frac{1}{r_{12}}\,\chi_t(1)\,\chi_u(2)\,d\tau_1\,d\tau_2 \quad ..2\text{-}22$$

The energy is now

$$E = \frac{1}{2}\sum_{r}^{\alpha}\sum_{s}^{\alpha}\left\{P_{rs}^{\alpha}\left(H_{rs}+F_{rs}^{\alpha}\right)\right\} + \frac{1}{2}\sum_{r}^{\beta}\sum_{s}^{\beta}\left\{P_{rs}^{\beta}\left(H_{rs}+F_{rs}^{\beta}\right)\right\} \qquad ..2\text{-}23$$

where

$$P_{rs}^{\alpha} = \sum_{i}^{\alpha} C_{ri}C_{si} \quad \text{and} \quad P_{rs}^{\beta} = \sum_{i}^{\beta} C_{ri}C_{si} \qquad ..2\text{-}24$$

The wavefunction used in this method - originally suggested by Pople and Nesbet, (34) - is, by previous considerations, not necessarily an eigen-function of S^2, (30). Further work has been done in order to try to form such an eigen-function, (35).

Spin Extended Hartree-Fock Theory:

The application of a spin projection operator, (36), O_S to a wavefunction can give a wavefunction which is an eigen-function of S^2.

$$\psi^S = O_S \psi \qquad ..2\text{-}25$$

The energy is calculated, using the spin eigen-function wavefunction as

$$E^S = \frac{\int \psi^S H \psi^S \, d\tau}{\int \psi^S \psi^S \, d\tau} \qquad ..2\text{-}26$$

The calculation of this energy is difficult, (37), and so an alternative method has been proposed, (38), where the energy is calculated using the unprojected wavefunction, ψ, and the result is then projected:

$$E = \frac{\int \psi H \psi \, d\tau}{\int \psi \psi \, d\tau} \qquad \text{..2-1}$$

$$E^S = O_S E \qquad \text{..2-27}$$

The validity of this method has been questioned, since the resulting energy is not necessarily a minimum, (39). Marshall , found that in certain cases the spin extended HF wavefunction gave a smaller energy lowering from the HF energy than the unrestricted energy.

Another suggestion to try to overcome the difficulties involved in the calculation of E^S by equation 2-26 is that, instead of the complete projection, O_S, an annihilator (40), A_S is used, (41). This annihilation operator removes the major contaminating spin state from the mixtures of states in the wavefunction, ψ.

The UHF wavefunction can be expanded in terms of wavefunctions that are eigen-functions of S^2,

where $S = \frac{1}{2}(n_\alpha - n_\beta)$

$$\psi = \sum_{m=0}^{\infty} C_{s+m} \psi_{s+m} \qquad \text{..2-28}$$

As m increases the value of the coefficients decreases, (48), thus the major contaminating spin component is (s + 1), (40).

After annihilation the wavefunction is

$$A_{S+1}\Psi = C_S \Psi_S + \sum_{m=2}^{n} C_{S+m} \Psi_{S+m} \quad ..2\text{-}29$$

This method has been applied successfully by Amos and Snyder (42,44); but it, too, has been criticised (43), since the physical quantities whose operators commute with the annihilation operator are not much changed by its application, (47).

II:5: Other Wavefunctions.

We shall now proceed to consider other wavefunctions, which, we hope will be as good, if not better than, the projected or annihilated HF ones.

Throughout this work we shall consider conjugated hydrocarbons. We shall construct molecular wavefunctions using only the pi-electrons of the molecule; the sigma-core, assumed constant, will be included in the Hamiltonian through the term $h_{core}(i)$. (For a comprehensive discussion of sigma - pi separability, see Parr (45) or Lykos and Parr (46).)

III. THE NON-PAIRED SPATIAL ORBITAL METHOD.

III.1:Introduction

It has been suggested that a wavefunction which makes some allowance for electron correlation could be formed by putting electrons of different spin into different spatial orbitals. The Non-Paired Spatial Orbital (NPSO) wavefunction is one type of DODS wavefunction, resulting from Linnett's work, (49).

The NPSO method starts from a valence bond (50) picture; but forms the molecular wavefunction from semi-localised two centre (nuclei) unsymmetrical bond orbitals, instead of from atomic orbitals.

NPSO calculations have been performed on, for example, the allyl radical, cation and anion, (51), benzene, (52), the nitrite ion, (53), and naphthalene, (54). This thesis is concerned with the extension of its application to a non-alternant hydrocarbon - azulene, large hydrocarbons - phenanthrene and anthracene, and open shell systems, such as the benzyl radical.

III.2: Linnett's Theory,(56).

Linnett suggested that the octet of electrons discussed by Lewis, (55), consisted of, not four groups of two electrons, but two groups of four electrons. His considerations of charge and spin effects lead him to this conclusion (56):-

"It is satisfactory, for a qualitative picture,

to think of the particles (electrons) in two sets, one set being made up of particles of one spin, and the other of the other spin. The most probable disposition of the particles is that in which the particles of each set adopt the most favourable disposition for that set, (opposite for two, equilateral triangle for three). If there are equal numbers of particles in each set, then the most probable configuration is that in which the particles are placed as pairs. If there are unequal numbers in each set, then the probability is independant of the mutual dispositions of the two sets."

In any many electron system, charge and spin effects must balance each other, since they have opposite effects. Electrons all have the same charge, therefore they repel each other. For two electrons of the same spin, which tend to keep apart due to spin effects, the charge correlation will be additive. But for two electrons of opposite spin, the spin pairing effect will cause them to interact, whereas charge considerations would cause them to repel each other.

Consider a group of eight electrons, four of α spin, and four of β spin. The charge effects within the set of α spin electrons will cause the electrons to arrange themselves so as to reduce inter-electronic repulsions. Thus they will be at the corners of a tetrahedron. The four β electrons will arrange themselves similarly. We now need to consider the relative positions of the two tetrahedra, since they will interact, to some extent, due to spin pairing.

In neon, for example, the filled shell contains eight electrons. Here the interaction between the two tetrahedra is probably quite weak; since there are no bonds the electrons will be positioned so as to minimise both charge and spin interactions.

In methane, CH_4, however, there are four directional bonds. Thus it is suggested that the two tetrahdra will interact quite strongly, due to spin pairing. Here it is immaterial whether the eight electrons are regarded as four pairs or two quartets.

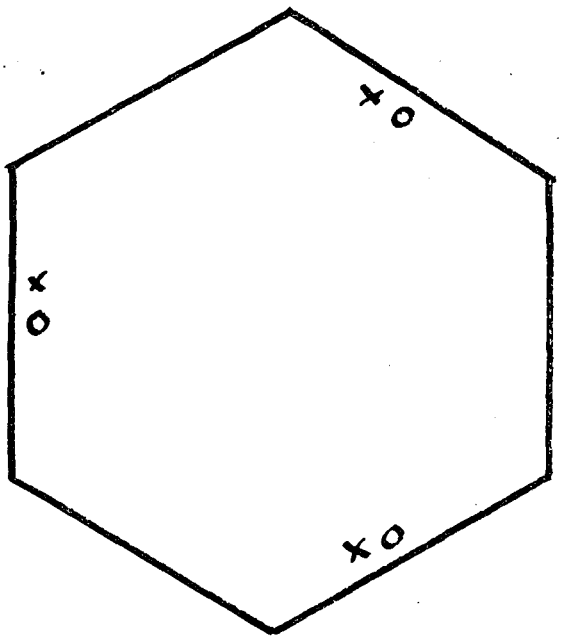
As an extension of this method to a pi-electron system, we chose the theoretical chemists' favourite molecule, benzene. This molecule has been closely studied by many workers, (e.g. 57,58,59), and has been considered in depth by Linnett and his co-workers,(52). Here the treatment is brief.

The six pi-electrons of benzene can be considered as two sets of three electrons, one set of α spin, the other of β spin. For the charge repulsion within the sets to be lowered the electrons will be spaced around a circle at 120°. (i.e. at the corners of an equilateral triangle.)

Now we must consider the relative correlations of the two sets.

Spin interactions suggest pairing - to give bonds, as in figure III-A.

Because of resonance we must include bonds as in figure III-B.

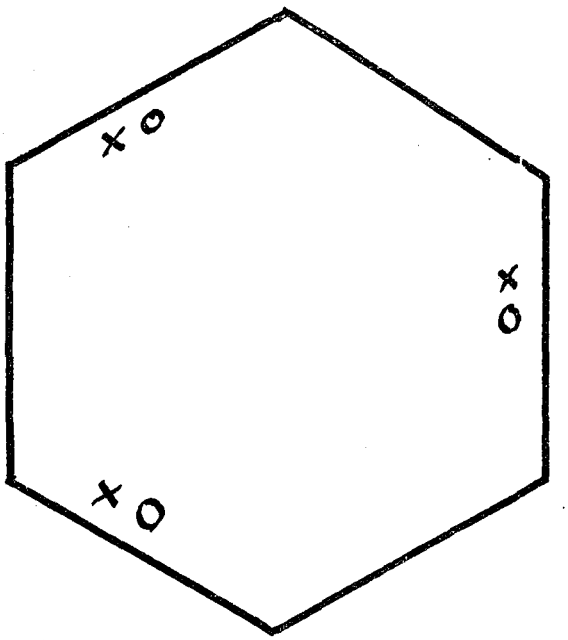


× denotes a one-electron bond containing a α spin electron

O denotes a one-electron bond containing a β spin electron.

Figure III-A

The electron spin arrangement of the benzene molecule.

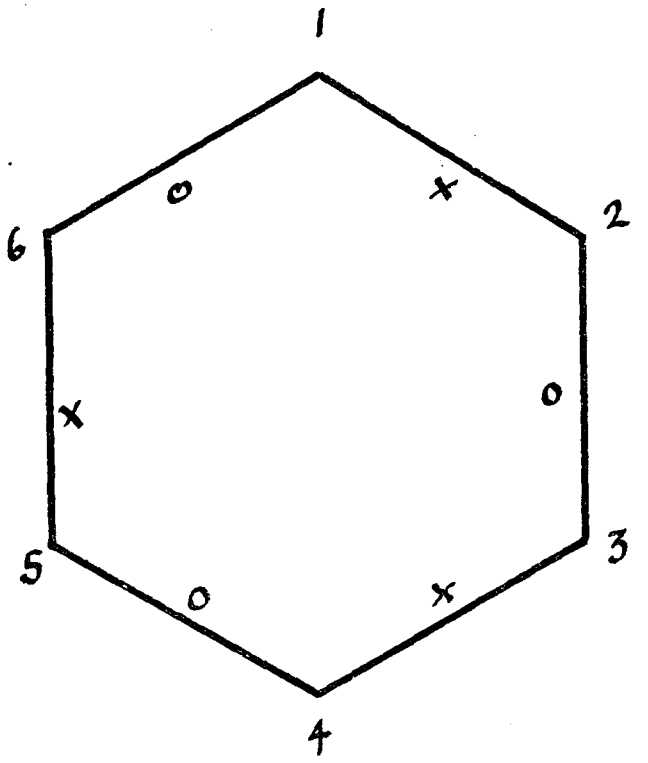


X denotes a one-electron bond containing a α spin electron.

O denotes a one-electron bond containing a β spin electron.

Figure III-B

The electron spin arrangement of the benzene molecule.



× denotes a one-electron bond containing a α spin electron.

o denotes a one-electron bond containing a β spin electron.

Figure III-C

The electron spin arrangement of the benzene molecule, different orbitals for different spins.

However charge correlation suggests that the arrangement of the two set will be as in figure III-C.

If spin interactions are more important than charge effects the wavefunction from arrangements III-A and III-B will give a lower energy than that from III-C; whereas if charge interactions are stronger than those of spin the wavefunction from arrangement III-C would give a lower energy.

Empedocles and Linnett (52) performed extensive calculations, on various models; their results led them to suggest that the best chemical formula for representing the electronic structure of benzene is as in figure III-C. This structure represents a situation in which electrons of different spins occupy different parts of space.

This NPSO[1] method has been applied to many systems. In all cases the wavefunctions so formed lower the ground state energy sufficiently to suggest that; (62)

" there is no particular and special energy effect involved in the 'pairing of electrons'. Therefore if there are two electrons and two bond regions, the best description of the system is as two one-electron bonds."

1. The method was originally called non-pairing, but renamed non-paired spatial orbital, in an effort to clarify the situation.

III.3:Formation of the NPSO Wavefunction.

a)

The major objective of the NPSO method is to form a molecular wavefunction in which electrons of opposite spin are separated as much as possible but at the same time maximising the bonding. Electrons are assigned to semi-localised bonding orbitals. From these a Slater determinant is formed such that adjacent one -electron bonds contain electrons of opposite spin.

The use of semi-localised orbitals was first suggested by Muller and Eyring (60) and Coulson and Fischer (61). Both replaced the atomic orbitals (χ_a and χ_b) in the molecular orbital wavefunction for hydrogen with orbitals of the type:-

$$\chi_1 = \chi_a + \lambda\chi_b$$

$$\chi_2 = \lambda\chi_a + \chi_b \qquad \text{..3-1}$$

Their calculations led them to conclude that ionic and covalent resonance can be equally well described by the introduction of asymmetrical orbitals,(61).

b)

As an example, the NPSO wavefunction for benzene is considered.

The NPSO wavefunction is constructed from two centre semi-localised orbitals, that span the bonding region of the molecule. The semi-localised orbitals are formed by combining adjacent 2p-pi atomic orbitals. For benzene, such a one-electron bond will be:-

$$(\chi_1 + k\chi_2)$$

where k is a variable parameter.

..3-2

If an electron of α spin is assigned to this semi-localised orbital, in order that correct separation of electron spins is achieved, the semi-localised orbitals

$$(\chi_2 + k\chi_3)$$

and

$$(\chi_6 + k\chi_1)$$

must contain electrons of β spin.

The complete wavefunction will be a Slater determinant of the form

$$\psi_1 = A\Big|(\chi_1+k\chi_2)(1)\,\alpha(1)\;(\chi_3+k\chi_4)(2)\,\alpha(2)\;(\chi_5+k\chi_6)(3)\,\alpha(3)\;(\chi_2+k\chi_3)(4)\,\beta(4)\;(\chi_4+k\chi_5)(5)\,\beta(5)\;(\chi_6+k\chi_1)(6)\,\beta(6)\Big|$$

..3-3

From the geometrical considerations, it may seem that for benzene, k would be equal to 1.0; but a rather inflexible wavefunction would result.

Now we have a wavefunction, equation 3-3, in which electrons of different spin occupy different spatial orbitals. However, it fails to satisfy the basic requi rements of an acceptable wavefunction.

c) Requirements for a satisfactory wavefunction:-

i) A satisfactory wavefunction must transform as one of the irreducible representations of the point group of the molecule.

By applying a symmetry projection operator, $\underline{P}_j$, (63), it is possible to meet this requirement.

The symmetry projection operator is defined as

$$\underline{P}_j = \frac{\ell_j}{h} \sum_r [\chi_{(j)}(R)]^* \underline{P}_R \qquad \ldots 3\text{-}4$$

where

j labels the irreducible representation

ℓ_j is the dimensionality of the representation

h is the order of the group

and

$\chi_{(j)}(R)$ is the character of the group operator, $\underline{P}_R$ for the j th. representation.

Effectively one needs to consider the results of applying the symmetry operations of the point group of the molecule to the initial wavefunction.

For example:-

Benzene has point group D_{6h}, with symmetry elements

E, C_2, C_3, i, S_3, S_6, σ_h, σ_v, σ_d.

Consider figure III-D. Under C_2 symmetry this gives figure III-E, and ψ_I (equation 3-3) becomes

$$A\,|(\chi_1+k\chi_6)(1)\alpha(1)\;(\chi_5+k\chi_4)(2)\alpha(2)\;(\chi_3+k\chi_2)(3)\alpha(3)\;(\chi_3+k\chi_1)(4)\beta(4)\;(\chi_6+k\chi_5)(5)\beta(5)\;(\chi_4+k\chi_3)(6)\beta(6)| = \psi_{II} \qquad ..3\text{-}5$$

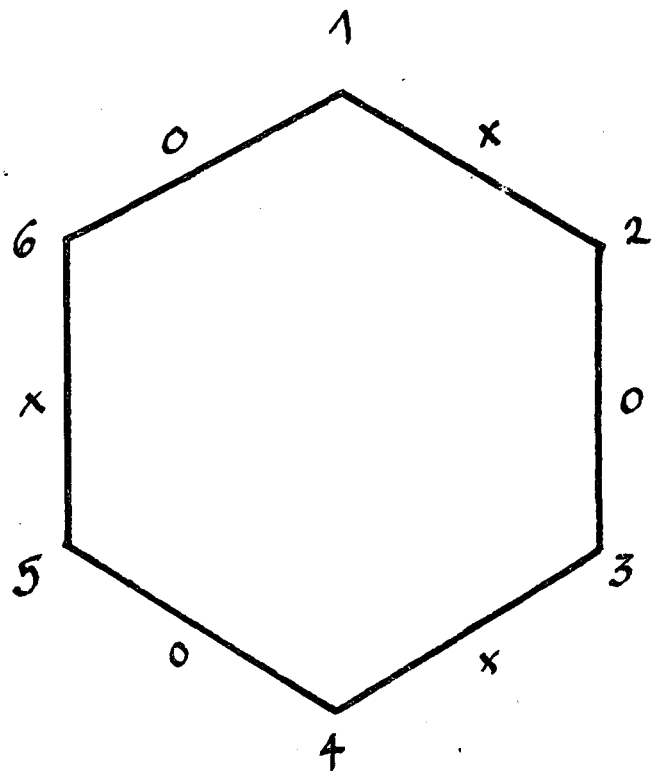
The application of the other symmetry elements to ψ_I will result in either ψ_{II}, or ψ_I or $\psi_{\bar{I}}$ with spins interchanged. For example: applying i gives figure III-F, and a wavefunction, ψ_{IV}, where

$$\psi_{IV} = A\,|(\chi_4+k\chi_5)(1)\alpha(1)\;(\chi_6+k\chi_1)(2)\alpha(2)\;(\chi_2+k\chi_3)(3)\alpha(3)\;(\chi_5+k\chi_6)(4)\beta(4)\;(\chi_1+k\chi_2)(5)\beta(5)\;(\chi_3+k\chi_4)(6)\beta(6)| \qquad ..3\text{-}6$$

which is $\psi_{\bar{I}}$ (equation 3-3) with α and β spins interchanged.

Defining ψ_{III} as ψ_{II} with α and β spins interchanged means the total wavefunction ψ_I is now

$$\psi_I = \psi_I + \psi_{II} - \psi_{III} - \psi_{IV}. \qquad ..3\text{-}7$$

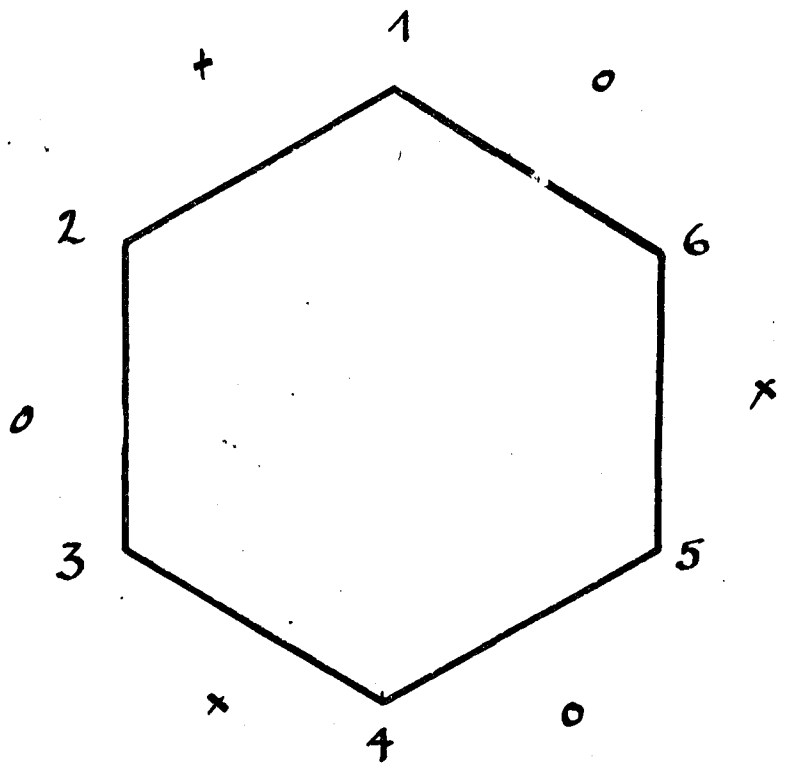


o denotes a one-electron bond containing an electron of β spin.

x denotes a one-electron bond containing an electron of α spin,

Figure III-D

The electron spin arrangement of the benzene molecule.

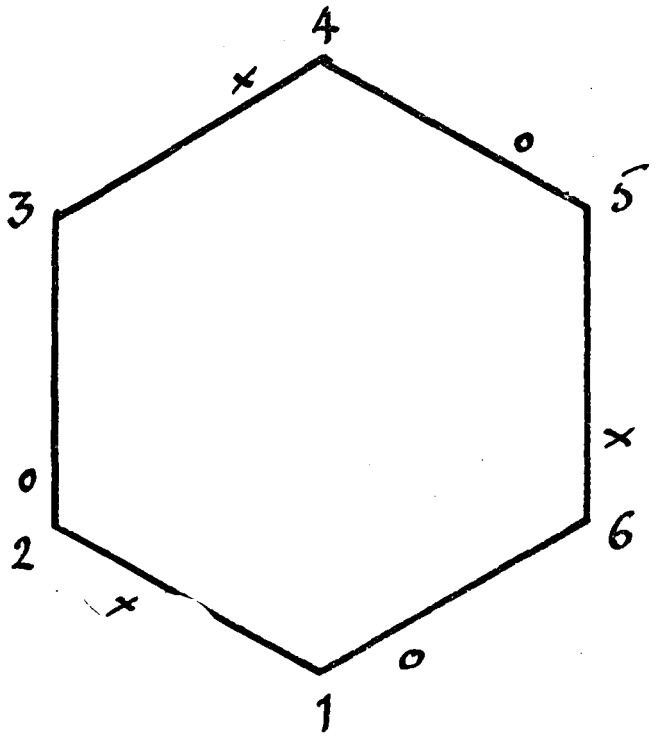


o denotes a one-electron bond containing an electron of β spin.

x denotes a one-electron bond containing an electron of α spin.

Figure III-E

The electron spin arrangement of the benzene molecule - under C_2 symmetry.



O denotes a one-electron bond containing an electron of β spin.

X denotes a one-electron bond containing an electron of α spin.

Figure III-F

The electron spin arrangement of the benzene molecule under i symmetry.

Requirements for a satisfactory wavefunction:-

ii)

The wavefunction ψ_T must be an eigen-function of the spin operators, S^2 and S_z.

i.e. $S^2 \psi_T = s(s+1)\,\psi_T$ ..3-8

By previous considerations, the NPSO wavefunction, (equation 3-7) is not necessarily an eigen-function of S^2. To make the wavefunction a pure spin state, singlet for benzene ground state, we must apply a spin projection operator, O_S, (19).

From equation 3-8 we get

$$(S^2 - s(s+1))\,\psi_T = 0 \qquad \text{..3-9}$$

Thus $(S^2 - s(s+1))$ will remove from the wavefunction, ψ_T, the term with spin component S. If $S = 0$, the singlet term will be annihilated; if $S = 1$ the triplet. By repeated application of O_S,

$$O_S = (S^2 - s(s+1)) \qquad \text{..3-10}$$

we can remove all terms except a specified one; say $S = k$. Thus

$$O_k = \prod_{j \neq k} \frac{S^2 - j(j+1)}{k(k+1) - j(j+1)} \qquad \text{..3-11}$$

(The inclusion of the denominator is to ensure the component with $S = k$ is unaltered.) The application of the operator, O_k, to a wavefunction, ψ, generates a spin eigen-function of multiplicity $2k + 1$.

Thus we must apply O_0 (k=0) to the NPSO wavefunction for benzene to obtain the singlet ground state.

$$O_0 = \prod_{j=1} \frac{S^2 - j(j+1)}{1 - j(j+1)} \qquad ..3\text{-}12$$

The resulting wavefunction is:

$$\psi = O_0 \psi_T \qquad ..3\text{-}13$$

or

$$\psi = O_0 (\psi_{\underline{I}} + \psi_{\underline{II}}) \qquad ..3\text{-}14$$

Here $\psi_{\underline{III}}$ and $\psi_{\underline{IV}}$ are included in the final wavefunction by the action of O_0 on $\psi_{\underline{I}}$ and $\psi_{\underline{II}}$, since $\psi_{\underline{III}}$ is obtained from $\psi_{\underline{II}}$ by three interchanges. That is

$$\psi_{\underline{III}} (\beta\beta\beta\,|\,\alpha\alpha\alpha) = - \psi_{\underline{II}} (\alpha\alpha\alpha\,|\,\beta\beta\beta) \qquad ..3\text{-}15$$

where $(\beta\beta\beta\,/\,\alpha\alpha\alpha)$

denotes that the first three semi-localised orbitals in the determinantal wavefunction contain β spin electrons, and the last three, α spin electrons. This can be written more compactly as

$$\psi_{\underline{III}} (\beta^3/\alpha^3) = - \psi_{\underline{II}} (\alpha^3/\beta^3) \qquad ..3\text{-}16$$

III.4:Calculation of the Ground State Energy.

i) Substituting equation 3-13 into equation I-3, the ground state energy, E, is

$$E = \frac{\int O_0 (\psi_{\underline{I}} + \psi_{\underline{II}}) H O_0 (\psi_{\underline{I}} + \psi_{\underline{II}}) \delta\tau}{\int O_0 (\psi_{\underline{I}} + \psi_{\underline{II}}) O_0 (\psi_{\underline{I}} + \psi_{\underline{II}}) \delta\tau} \qquad ..3\text{-}19$$

Using the properties of projection operators,(19), idempotency and commutation with the Hamiltonian operator, this reduces to

$$E = \frac{\int (\psi_I + \psi_{II}) H O_0 (\psi_I + \psi_{II}) \delta\tau}{\int (\psi_I + \psi_{II}) O_0 (\psi_I + \psi_{II}) \delta\tau} \qquad ..3\text{-}18$$

The energy calculation now reduces to two problems; calculation of integrals of the type $\int \psi_I H O_0 \psi_I \delta\tau$ and of the type $\int \psi_I H O_0 \psi_{II} \delta\tau$, and the corresponding overlap integrals,

$$\int \psi_I O_0 \psi_I \delta\tau \quad , \qquad ..3\text{-}19$$

and

$$\int \psi_I O_0 \psi_{II} \delta\tau$$

ii) Calculation of $\int \psi_I H O_S \psi_I \delta\tau$

Since the operation of O_S on the wavefunction ψ_I , produces a new wavefunction that is a linear combination of Slater determinants, then the calculation of $\int \psi_I H O_S \psi_I \delta\tau$ is complex.

The value of the energy of a projected single determinant can be calculated more easily if the orbitals can be transformed to either the "corresponding orbitals" of Amos and Hall, (64),or the "paired orbitals"of Löwdin,(65). Consider two sets of orbitals: u_i of α spin and v_i of β spin, If the sets $u_1, u_2, \ldots\ldots u_n$ and $v_1, v_2, \ldots v_n$ are linearly independent there exists a non-singular transformation, which will transform them into orthogonal orbitals, $u_1', u_2', \ldots\ldots u_n'$ and $v_1', v_2', \ldots\ldots v_n'$.

$$u_i' = \sum_k u_k U_{ki} \qquad ..3\text{-}20$$

such that

$$\int u_i' u_j' \, d\tau = \delta_{ij} \qquad ..3\text{-}21$$

A determinantal wavefunction formed from the orbitals u_i' differ from that formed by the initial orbitals u_i, by a factor $\det|U|$. The same type of transformation holds for the set v_i.

$$v_i' = \sum_k v_k V_{ki} \qquad ..3\text{-}22$$

$$\int v_i' v_j' \, d\tau = \delta_{ij} \qquad ..3\text{-}23$$

Thus it is possible to form an orthonormal set of orbitals from any linearly independent set of orbitals, without essentially changing the HF wavefunction.

Now we must consider the relationships between the two sets, u_i' and v_i'. If we could construct the sets such that

$$\int u_i' v_j' \, d\tau = \lambda_i \delta_{ij}, \qquad ..3\text{-}24$$

that is such that the overlap matrix contains only diagonal and pseudo-diagonal terms, the number of non-vanishing integrals in the energy calculation $\int \psi_I H O_s \psi_I \, d\tau$ would be considerably reduced. This "pairing theorem" was formulated by Amos and Hall, (64) and Löwdin, (65).

The overlap matrix between the two sets can be formed

$$D_{ij} = \langle u_i' | v_j' \rangle \qquad ..3\text{-}25$$

$\langle u_i' | v_j' \rangle$ is equivalent to $\int u_i' v_j' \, d\tau$.(66)

Two transforms are now required

$$a_i = \sum_k u'_k A_{ki}$$
$$b_j = \sum_l v'_l B_{lj} \qquad ..3\text{-}26$$

such that

$$\langle a_i | b_j \rangle = \lambda_i \delta_{ij} \qquad ..3\text{-}27$$

$$\sum_k \sum_l A^*_{ki} \langle u'_k | v'_l \rangle B_{lj} = \lambda_i \delta_{ij} \qquad ..3\text{-}28$$

i.e.

$$A^* B D = \Lambda, \qquad \Lambda \text{ diagonal.}$$

Multiplying by Λ^*, the adjoint of Λ,

$$\Lambda^* = B^* D^* A \qquad ..3\text{-}29$$

gives

$$A^* D B B^* D^* A = \Lambda \Lambda^* \qquad ..3\text{-}30$$

But $B B^* = E$, the unit matrix.

Thus

$$A^* (D D^*) A = \Lambda \Lambda^* \qquad ..3\text{-}31$$

Thus A can be found by considering the diagonalisation of $(D D^*)$, which is Hermitian. Thus, generally, we can require the following orthogonality conditions of any two sets of orbitals:-

$$\langle u_i | u_j \rangle = \delta_{ij}$$
$$\langle v_i | v_j \rangle = \delta_{ij} \qquad ..3\text{-}32$$
$$\langle u_i | v_j \rangle = \lambda_i \delta_{ij}$$

We can now go on to calculate the values of the integrals $\int \psi_I H O_S \psi_I \delta\tau$ and $\int \psi_I O_S \psi_I \delta\tau$, by well-documented methods, (67,68). We chose to follow that of Pauncz,(67) for closed shell molecules, and that of Harris, (68) for open shell systems.

By considering the effects of the antisymmetriser on the space and spin parts of the wavefunction, Pauncz wrote the matrix elements of H, and the overlap matrix as:

$$\langle \psi_k | H | \psi_\ell \rangle = \sum_P (-1)^P H(P)\, U(P)_{k\ell}$$

$$\langle \psi_k | \psi_\ell \rangle = \sum_P (-1)^P I(P)\, U(P)_{k\ell} \qquad \text{..3-33}$$

where

$$U(P)_{k\ell} = \langle \chi_k | P^\sigma \chi_\ell \rangle$$

$$H(P) = \langle \phi | H | P^r \phi \rangle$$

$$I(P) = \langle \phi | P^r \phi \rangle \qquad \text{..3-34}$$

χ denotes spin function,

P^σ denotes permutation of spin function

P^r denotes permutation of space function.

Now projecting the spin function gives,

$$\langle \psi_k | H | \psi_\ell \rangle = \sum_P (-1)^P H(P)\, C(s,q)$$

$$\langle \psi_k | \psi_\ell \rangle = \sum_P (-1)^P I(P)\, C(s,q) \qquad \text{..3-35}$$

Where $C(s,q) = \langle \Phi_k | P^6 \Phi_\ell \rangle$

Φ_k and Φ_ℓ are projections of products of γ_k and χ_ℓ spin functions, Θ_k and Θ_ℓ.

and where

$$\Phi_1 = O_S \Theta_1 = \sum_{i=0}^{n} C(s,i) T_i$$

$$T_i = [\alpha^{n-i} \beta^i][\alpha^i \beta^{n-i}] \qquad ..3\text{-}36$$

and q is the characteristic number. All functions with the same T_i, that is, all those functions which have i β - functions amongst the first n α - functions will have the same characteristic number, q.

From these equations and the orthogonality relationships between paired orbitals, equation 3-27, we can write the overlap as,

$$\langle \psi | \psi \rangle = \Lambda_0^S = \sum_{k=0}^{n} (-1)^k S_k \; C(s,k) \qquad ..3\text{-}37$$

where S_k are the symmetric sums, such that

$$\begin{aligned} S_0 &= 1, \\ S_1 &= \sum_i x_i \\ S_2 &= \sum_{i<j} x_{ij} \\ &\cdots \qquad S_n = x_1 x_2 x_3 \cdots \cdots x_n \end{aligned} \qquad ..3\text{-}38$$

and $C(s,k)$ are defined $(_{67})$ as , if s = 0,

$$C_k = \frac{(-1)^k}{n+1} \binom{n}{k}^{-1} \qquad ..3\text{-}39$$

and, if s = 1,

$$C_k = \frac{(-1)^k 3}{(n+1)(n+2)} \binom{n}{k}^{-1} (n-2k). \quad ..3\text{-}40$$

The one electron part of the energy is now

$$\langle \Psi | H_1 | \Psi \rangle = \sum_{i=1}^{n} \{ \langle I | h | I \rangle + \langle \bar{I} | h | \bar{I} \rangle \} \sum_{k=0}^{n-1} (-1)^k {}^{i}S_k \, C(s,k$$

$$+ \sum_{i=1}^{n} \{ \langle I | h | \bar{I} \rangle \lambda_i^* + \langle \bar{I} | h | I \rangle \lambda_i \} \sum_{k=0}^{n-1} (-1)^{k+1} {}^{i}S_k \, C(s,k+1) \quad ..3\text{-}41$$

where

i) $$\langle I | h | I \rangle = \int a_I^*(i) \, h(i) \, a_I(i) \, \delta v_i \quad ..3\text{-}42$$

ii) $$\langle I | h | \bar{I} \rangle = \int a_I^*(i) \, h(i) \, \bar{a}_I(i) \, \delta v_i \quad ..3\text{-}43$$

iii) $${}^{i}S_k = \frac{d}{dx_i} S_{k+1} = S_k - x_i \frac{d}{dx_i} S_k \quad ..3\text{-}44$$

iv) $$\lambda_i = \int a_I(i) \, \bar{a}_I(i) \, \delta v_i \quad ..3\text{-}45$$

where a_I and $\bar{a}_I$ are paired orbitals.

The two electron part of the energy is given by equation 3-46, where

$$\langle ik | jl \rangle = \int a_i^*(1) \, a_j^*(2) \, \frac{e^2}{r_{12}} \, a_k(1) \, a_l(2) \, \delta v_1 \, \delta v_2 \quad ..3\text{-}47$$

and ..3-48

$${}^{ij}S_k = \frac{d^2}{dx_i \, dx_j} S_{k+2}$$

$$\langle\psi|\sum_{i<j}^{n}\left\{\frac{e^2}{r_{ij}}+\frac{e^2}{r_{n+i,n+j}}+\frac{e^2}{r_{n+i,j}}+\frac{e^2}{r_{i,n+j}}\right\}|\psi\rangle =$$

$$\sum_{i<j}\Bigg\{\Big[(ii|jj)+(ii|\bar{j}\bar{j})+(\bar{i}\bar{i}|jj)+(\bar{i}\bar{i}|\bar{j}\bar{j})-(ij|ji)-(\bar{i}\bar{j}|\bar{j}\bar{i})\Big]\sum_{k=0}^{n-2}(-1)^k\,{}^{ij}S_k\,C_{(s,k)}$$

$$-\Big[\lambda_i\{(ij|\bar{j}\bar{i})+(\bar{i}\bar{j}|\bar{j}\bar{i})+(\bar{i}j|ji)+(i\bar{j}|\bar{j}\bar{i})-(i\bar{i}|jj)-(\bar{i}i|\bar{j}\bar{j})-(\bar{i}i|jj)-(i\bar{i}|\bar{j}\bar{j})\}$$

$$+\lambda_j\{(i\bar{j}|ji)+(\bar{i}j|\bar{j}\bar{i})+(\bar{i}\bar{j}|j\bar{i})+(ij|\bar{j}i)-(ii|j\bar{j})-(\bar{i}\bar{i}|\bar{j}j)-(\bar{i}\bar{i}|j\bar{j})-(ii|\bar{j}\bar{j})\}$$

$$-\{(\bar{i}j|j\bar{i})+(i\bar{j}|\bar{j}i)\}-\lambda_i\lambda_j\{(\bar{i}\bar{j}|ji)+(ij|\bar{j}\bar{i})\}\Big]\sum_{k=0}^{n-2}(-1)^k\,{}^{ij}S_k\,C_{(s,k+1)}$$

$$+\Big[(i\bar{i}|j\bar{j})+(\bar{i}i|\bar{j}j)+(\bar{i}i|j\bar{j})+(i\bar{i}|\bar{j}j)-(i\bar{j}|j\bar{i})-(\bar{i}j|\bar{j}i)\Big]\lambda_i\lambda_j\sum_{k=0}^{n-2}(-1)^k\,{}^{ij}S_k\,C_{(s,k+2)}\Bigg\}$$

..3-46

This formula is misquoted in Pauncz,(67), equation 3.96 in this reference, since there should be a negative sign before the penultimate square bracket term.

Again $i,(j)$ and $\bar{i},(\bar{j})$ are paired orbitals.

iii) Calculation of $\int \psi_I |H| O_S \psi_{II} \, d\tau$

There is, to our knowledge, no easy way of calculating integrals of the type $\int \psi_I |O_S \psi_{II} \, d\tau$ and $\int \psi_I |H| O_S \psi_{II} \, d\tau$, when ψ_I and ψ_{II} have different non-orthogonal spatial parts, because they have no pairing properties. Thus a prohibitive number of permutations have to be included in equation 3-35. This is also true of the method of Gerrard and Lipscomb,(69). This is the major hurdle in the NPSO method. Duke(73) attempted to overcome the difficulty of lack of orthogonality between the functions used to construct the NPSO wavefunction by using orthogonalised atomic orbitals to construct the semi-localised one-electron bonds used in the determinant. The results were somewhat disappointing. He found the molecular orbital wavefunction was invariant under transformation to the orthogonalised atomic orbital (OAO) basis, the AMO wavefunction was improved by such a transformation, but the NPSO wavefunction worsened.

It is possible to calculate each integral between separate determinants by the method of King et al,(70); but this would be rather tedious and time consuming. For example $O_S \psi_{II}$, for a ten electron system would be a combination of 852 determinants. Using an annihilation operator (see section II.4) in place of a projection operator reduces the amount of work involved considerably. Here $A_{S+1} \psi_{II}$ for a ten electron system is a combination of 52 determinants. The integrals reduce thus;-

$\langle \psi_I | H | O_S \psi_{II} \rangle$ to $\langle \psi_I | H | A_{S+1} \psi_{II} \rangle$

$\langle \psi_I | H | O_S \psi_I \rangle$ to $\langle \psi_I | H | A_{S+1} \psi_I \rangle$

III.5:Energy Calculations.

Because of the difficulties of applying the projected NPSO method various approximate methods have been used.

i)
Unprojected NPSO.

Here equations of the type 3-7 are used.

$$E = \frac{\langle \psi_I + \psi_{II} - \psi_{III} - \psi_{IV} | H | \psi_I + \psi_{II} - \psi_{III} - \psi_{IV} \rangle}{\langle \psi_I + \psi_{II} - \psi_{III} - \psi_{IV} | \psi_I + \psi_{II} - \psi_{III} - \psi_{IV} \rangle}$$

$$= \frac{\langle \psi_I|H|\psi_I\rangle + \langle \psi_I|H|\psi_{II}\rangle + \langle \psi_I|H|\psi_{III}\rangle + \langle \psi_I|H|\psi_{IV}\rangle}{\langle \psi_I|\psi_I\rangle + \langle \psi_I|\psi_{II}\rangle + \langle \psi_I|\psi_{III}\rangle + \langle \psi_I|\psi_{IV}\rangle} \quad ..3\text{-}49$$

ii)
Annihilated NPSO.

Here an annihilation operator was used - instead of a projection operator. The method was a modification of the annihilation proposed by Amos and Hall,(40). The energy was calculated using:-

$$E = \frac{\langle \psi_I | H | A_{s+1} \psi_I \rangle + \langle \psi_J | H | A_{s+1} \psi_J \rangle}{\langle \psi_I | A_{s+1} \psi_I \rangle + \langle \psi_I | A_{s+1} \psi_J \rangle} \quad ..3\text{-}50$$

The Pauncz formulae, equations 3-37, 3-41, 3-46, were used to calculate the integrals $\langle \psi_I | H | A_{s+1} \psi_I \rangle$ and $\langle \psi_I | A_{s+1} \psi_I \rangle$ with suitable coefficients in the expansion

$$O_s \psi = \sum_{i=0}^{n} C_{(s,i)} T_i \quad ..3\text{-}51$$

We used the terms for which i = 1 and i = 0,(and the comparable interchanges of spin, i = n, and i = n-1), denoting permutation of one or no α spin electrons amongst the β spin ones, (and n or n-1). All other terms were annihilated by setting $C(s,i)$ for $n-1 > i > 1$ equal to zero.

For the terms $\langle \psi_I | H | A_{s+1} \psi_{\bar{J}} \rangle$ and $\langle \psi_I | A_{s+1} \psi_{\bar{J}} \rangle$ the integrals were calculated directly between Slater determinants in which the required numbers of α - spin electrons had been permuted amongst the β- ones, with a maximum number of one, for annihilation.

iii)

Projected and Unprojected NPSO

Here a further approximation was used, in place of annihilation, to investigate how close to that of equation 3-50 an approximate energy can be calculated, with, optimistically, a good reduction in computing time. The fully spin projected formula was used for the single determinant terms; whereas only the first and last terms in the expansion 3-51 were included from the term $\langle \psi_i | H | O_s \psi_{\bar{J}} \rangle$.

$$E = \frac{\langle \psi_I | H | O_s \psi_I \rangle + \langle \psi_I | H | \psi_{\bar{J}} \rangle + \langle \psi_I | H | \psi_{\bar{w}} \rangle}{\langle \psi_I | O_s \psi_I \rangle + \langle \psi_I | \psi_{\bar{J}} \rangle + \langle \psi_I | \psi_{\bar{w}} \rangle} \quad \text{..3-52}$$

iv)

Projected and Annihilated NPSO.

Again the fully projected formula was used for the single determinant term. The annihilation procedure was used for the cross term between the two determinants; $\langle \Psi_I | H | O_S \Psi_{II} \rangle$ was reduced to $\langle \Psi_I | H | A_{S+1} \Psi_{II} \rangle$.

Hopefully the results of this calculation should be near to those expected for complete projection.

$$E' = \frac{\langle \Psi_I | H | O_S \Psi_I \rangle + \langle \Psi_I | H | A_{S+1} \Psi_{II} \rangle}{\langle \Psi_I | O_S \Psi_I \rangle + \langle \Psi_I | A_{S+1} \Psi_{II} \rangle} \quad \text{..3-53}$$

All four approximations were applied to the azulene molecule.

IV. AZULENE.

IV.1:Introduction.

Since the previous NPSO calculations on hydrocarbons have been on alternant systems it seemed natural to try to extend the method to a non-alternant system. Pauncz and his co-workers(71) have investigated, quite thoroughly the application of a comparable DODS method, the AMO method, to azulene. This work uses their integral values, and the same geometry, so that a direct comparision of their results, with ours, is possible.

IV.2: The Alternant Molecular Orbital Method, AMO, method.

The AMO method is a DODS method, originally proposed for alternant hydrocarbons. It was Slater,(72) who originally suggested that electrons having different spin, in alternant systems, may be in orbitals localised on different atoms.

For alternant hydrocarbons, the Hückel molecular orbitals are paired, such that a bonding MO, ψ_i, of energy $\alpha - x_i\beta$ is matched by an anti-bonding MO, $\bar{\psi}_i$, of energy $\alpha + x_i\beta$. (Here $\alpha = \langle \chi_r | H_{eff} | \chi_r \rangle$ and $\beta = \langle \chi_r | H_{eff} | \chi_s \rangle$.) Using equation 3-27, any set of orthonormal orbitals can be paired. The AMO method combines these paired orbitals to form new localised AMO's, alternant molecular orbitals.

From $\bar{\psi}_i$ and $\bar{\psi}_{\bar{i}}$ the new orbitals u_i and v_i are formed thus,

$$u_i = \cos\theta_i \bar{\psi}_i + \sin\theta_i \bar{\psi}_{\bar{i}}$$
$$v_i = \cos\theta_i \bar{\psi}_i - \sin\theta_i \bar{\psi}_{\bar{i}} \qquad ..4\text{-}1$$

$0 \leq \theta \leq \frac{1}{4}\pi$

These orbitals satisfy equation3-27 such that

$$\langle u_i | v_i \rangle = \cos 2\theta_i = \lambda_i \qquad ..4\text{-}2$$

If $\theta_i = 0$ then the AMO's are the original doubly occupied MO's.

If α electrons are assigned to the u_i set and β electrons to the v_i set we can form a determinantal wavefunction that has different spatial orbitals for different spins.This wavefunction must be spin projected to bring it to a pure spin state. This projected wavefunction can be used to calculate the AMO energy, using equations 3-37,3-41,3-46. This is, in fact, the "many parameter"AMO method; by setting all $\theta_i = \theta$ the AMO method can be reduced to a one parameter method.

Although the method was originally developed for alternant hydrocarbons, it has now been extended to non-alternant hydrocarbon molecules. However the pairing needs special attention - it is not satisfactory to just pair the lowest MO with the highest, symmetry considerations must be taken into account.To give further improvement in the results, transformations can be performed among the unoccupied orbitals, leading to what we will refer to as the "optimised AMO method".

IV.3: The NPSO Method.

The geometry of the azulene molecule is shown, with the numbering scheme, in figure IV-A.

The NPSO wavefunction is constructed from the 2p - pi orbitals, χ_i , on the carbon atoms. For azulene there are ten pi-electrons, but eleven bonds. Since the NPSO one-electron bonds span the bonding region, we have a choice as to which bonds to use. From the geometry, the 3 - 9 bond is the longest, of length 1.483 Å. It is almost comparable to the suggested sp^2- sp^2 bond length, (73),of 1.5 Å, so it was thought that the exclusion of the 3 - 9 bond would not be too serious. Hence the NPSO wavefunction was written so as to span the bonds

(1 - 2), (2 - 3), (3 - 4), (4 - 5), (5 - 6),
(6 - 7), (7 - 8), (8 - 9), (9 - 10), (10 - 1),

as

$$\psi_1 = A\Big|\ (\chi_1+k\chi_2)(1)\,\alpha(1)\ (\chi_3+k\chi_4)(2)\,\alpha(2)$$
$$(\chi_5+k\chi_6)(3)\,\alpha(3)\ (\chi_7+k\chi_8)(4)\,\alpha(4)$$
$$(\chi_9+k\chi_{10})(5)\,\alpha(5)\ (\chi_2+k\chi_3)(6)\,\beta(6)$$
$$(\chi_4+k\chi_5)(7)\,\beta(7)\ (\chi_6+k\chi_7)(8)\,\beta(8)$$
$$(\chi_8+k\chi_9)(9)\,\beta(9)\ (\chi_{10}+k\chi_1)(10)\,\beta(10)\Big| \qquad \text{..4-3}$$

where k is a variable parameter.

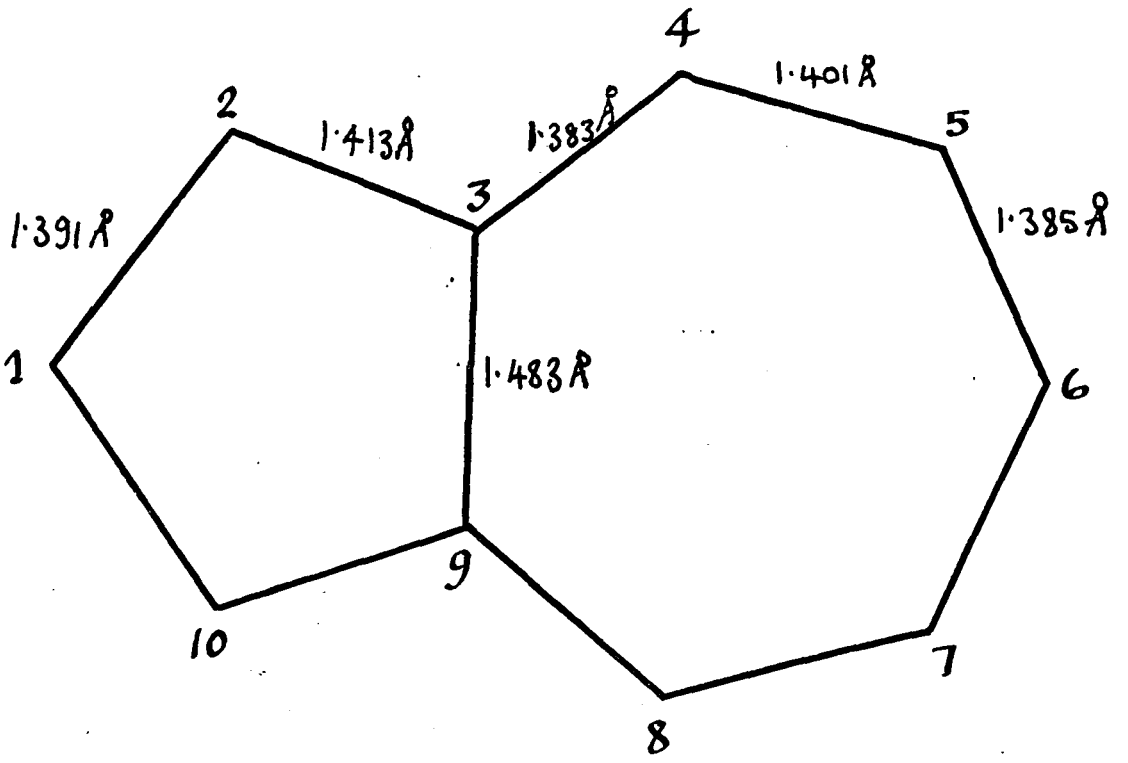


Figure IV-A

The geometry and numbering for the azulene molecule.

As with benzene, a symmetry projection operator must be applied in order to give a wavefunction of the correct symmetry.

The point group of the azulene molecule is C_{2v}, and the ground state belongs to the A_1 representation. This gives the total wavefunction as

$$\psi_T = (\psi_I + \psi_{II}) \qquad \text{..4-4}$$

where

$$\psi_{II} = A\,|\,(k\chi_1+\chi_2)(1)\beta(1)\ (\chi_4+k\chi_3)(2)\beta(2)\ (k\chi_5+\chi_6)(3)\beta(3)\ (\chi_8+k\chi_7)(4)\beta(4)\ (k\chi_9+\chi_{10})(5)\beta(5)\ (k\chi_2+\chi_3)(6)\alpha(6)\ (k\chi_4+\chi_5)(7)\alpha(7)\ (k\chi_6+\chi_7)(8)\alpha(8)\ (k\chi_8+\chi_9)(9)\alpha(9)\ (k\chi_{10}+\chi_1)(10)\alpha(10)\,|$$

Application of a singlet projection operator gives a wavefunction with the correct spin properties:-

$$\psi_S = O_0(\psi_I + \psi_{II}) \qquad \text{..4-6}$$

IV.4:Calculations.

The atomic integrals used, those of Pauncz, are quoted in table IV-1.

Integral values for the Azulene molecule.

element	coulomb integral	overlap integral	matrix element of the Hamiltonian.
11	17.22895	1.0	-70.7492
22			-72.4425
33			-83.2369
44			-74.6715
55			-71.6832
66			-70.4674
12	9.07432	0.25052	-20.1577
23	8.96533	0.24036	-20.6733
34	9.11449	0.25387	-22.1346
45	9.02452	0.24636	-20.1818
56	9.10442	0.25302	-20.2111
39	8.63228	0.21438	-19.3412
13	6.15138	0.05438	-3.8090
14	3.95910	0.00279	-0.1853
15	3.03072	0.00018	-0.0114
16	2.75890	0.00005	-0.0035
24	5.55538	0.03147	-2.1182
25	3.72081	0.00159	-0.1045
26	3.10022	0.00023	-0.0151
27	3.16400	0.00029	-0.0194
28	3.81940	0.00203	-0.1362
29	5.83321	0.04126	-2.9283
2 10	5.80178	0.04008	-2.6557
35	5.51863	0.03029	-2.1365
36	4.41478	0.00682	-0.4765

table IV-1, continued.

element	coulomb integral	overlap integral	matrix element of Hamiltonian
37	4.46132	0.00739	-0.5209
38	5.35313	0.02531	-1.8231
46	5.41308	0.02706	-1.7912
47	4.48563	0.00770	-0.5146
48	4.39903	0.00664	-0.4536
57	5.64088	0.03432	-2.2438

Table IV-1.

As a reference energy, we calculated the molecular orbital energy, by equation 2-3, using the eigenvectors of the overlap matrix as molecular orbitals. We were unable to obtain exact agreement with the MO energy, or eigenvectors, quoted by Pauncz, (74) or Silberman, (71), so their values are also quoted. The eigenvectors of the overlap matrix are given in table IV-2.

We performed an SCF-MO energy calculation, using Roothaan's method, (see section II-3). These results are also given, with the SCF-MO's, in table IV-3.

The AMO results are also quoted. The AMO method has been applied to azulene as a one parameter method, (75), a five parameter method, (75), and in its optimised form, (71), in which, in addition to the five parameters previously used, orthogonal transformations were carried out amongst the anti-bonding orbitals, using an iterative procedure. All results are given in table IV-4.

For the unprojected calculations, using the NPSO method, we used a wavefunction that included interchange of spins in ψ_I and ψ_{II} ; that is:-

$$\psi_T = \psi_I + \psi_{II} - \psi_{III} - \psi_{IV} \qquad \text{..4-7}$$

where

ψ_{III} is given by interchanging the spins of ψ_I, and

ψ_{IV} is given by interchanging the spins of ψ_{II}.

Eigenvectors of the overlap matrix for azulene.

atom no.	1	2	3	4	5	6	symmetry.
molecular orbital							
1	0.2460	0.2572	0.3356	0.2230	0.1675	0.1499	B_2
2	-0.2870	-0.2324	-0.0943	0.1562	0.3569	0.4285	B_2
3	0.0	-0.1828	-0.2643	-0.4267	0.3062	0.0	A_2
4	-0.4941	-0.2173	0.3285	0.2626	-0.1439	-0.3736	B_2
5	0.0	-0.5298	-0.2520	0.1407	0.3378	0.0	A_2
6	0.3945	-0.0580	-0.3653	0.4762	0.1348	-0.5312	B_2
7	0.0	0.3682	-0.2670	-0.3764	0.5353	0.0	A_2
8	-0.7340	0.5887	-0.2026	-0.0535	0.2705	-0.3538	B_2
9	-0.2371	0.2528	-0.2569	0.4418	-0.5676	0.6260	A_2
10	0.0	0.3172	-0.7186	0.4806	-0.2388	0.0	A_2

Table IV-2.

SCF - LCAO Molecular orbitals for Azulene.

atom no.	1	2	3	4	5	6	symmetry
molecular orbital							
1	0.0232	0.0645	0.2095	0.2738	0.3446	0.3853	B_2
2	0.0	0.1841	0.3242	0.3914	0.2990	0.0	A_2
3	0.2620	0.2677	0.3427	0.0902	-0.2143	-0.3433	B_2
4	0.5916	0.3018	-0.2952	-0.1941	0.1016	0.2490	B_2
5	0.0	0.4164	0.3505	-0.1517	-0.4090	0.0	A_2
6	0.2983	-0.0729	-0.3549	0.4996	0.1355	-0.5568	B_2
7	0.0	0.4476	-0.2188	-0.3961	0.4753	0.0	A_2
8	0.6005	-0.4522	0.0714	0.2274	-0.4600	0.5532	B_2
9	0.0	-0.3778	0.6673	-0.4914	0.2622	0.0	A_2
10	0.5186	-0.4522	0.3005	-0.3818	0.4299	-0.4477	B_2

Table IV-3

The annihilated NPSO energy was calculated using equation 3-50; the projected and annihilated energy by equation 3-53. The projected and unprojected calculation was performed using equation 3-52; here as in the unprojected NPSO calculations, we included interchange of spins for ψ_{II} , the interchange of spins for ψ_{I} being included through the use of the spin projection operator.

All minimum energy values, and corresponding k - values are quoted in table IV-4.

IV.5: Results.

The results show that, even without full spin projection, the NPSO method compares favourably with the AMO method. The simplest NPSO calculation - unprojected NPSO - is appreciably better than the five parameter AMO calculation. The annihilated form of the NPSO method, (equation 3-50), gives a lower energy than the more complex optimised AMO method of Silberman. We thus conclude that the NPSO method successfully allows for electron correlation for azulene.

By considering the results of the various NPSO approximations, and the minimum values of k, we also suggest that equation 3-52

$$E = \frac{\langle\psi_I|H|\Omega_S\psi_I\rangle + \langle\psi_I|H|\psi_{II}\rangle - \langle\psi_I|H|\psi_{IV}\rangle}{\langle\psi_I|\Omega_S\psi_I\rangle + \langle\psi_I|\psi_{II}\rangle - \langle\psi_I|\psi_{IV}\rangle}$$

gives an energy that will be a reasonable approximation to that of full spin projection. On the basis of

Results of the energy calculations for Azulene.

results quoted in e.V.

method	energy	k
MO, using eigenvectors of the overlap matrix.		
Pauncz [1]	-490.0192 e.V.	
Silberman et al [2]	-490.0606 e.V.	
this work	-490.0134 e.V.	
SCF-LCAO-MO	-490.7623 e.V.	
AMO (1 parameter) [1]	-491.9428 e.V.	
AMO (5 parameters) [1]	-493.1266 e.V.	
unprojected NPSO	-494.4050 e.V.	0.2555
projected and unprojected NPSO	-495.2340 e.V.	0.2273
optimized AMO [2]	-495.3652 e.V.	
annihilated NPSO	-495.5472 e.V.	0.23
projected and annihilated NPSO	-495.8820 e.V.	0.228

If k = 0.25, the following results are obtained:-

projected and unprojected NPSO	-495.2050 e.V.
annihilated NPSO	-495.5230 e.V.
projected and annihilated NPSO	-495.8516 e.V.

[1] reference 75,

[2] reference 71.

Table IV-4.

calculations on several hydrocarbon pi-electron systems Empedocles and Linnett (76) suggested that no serious errors would be introduced by putting $k = 0.25$; and that using this approximation it should be possible to write reasonably accurate NPSO wavefunctions for large hydrocarbon molecules. The energies of the various NPSO approximations quoted give further support to this idea.

Perhaps here further comment should be made on the non-inclusion of the 3 - 9 bond, the bridge bond, in the NPSO wavefunction. Comparable calculations on naphthalene have been performed, (78). It was observed that the NPSO method results were not as good as those of even the one-parameter AMO method. The reason suggested for this, was the neglect of the 9 - 10, bridge bond in the NPSO wavefunction. With this in mind it might seem an anomaly that, in azulene, the bridge bond was not considered, and yet the method was very successful. However in naphthalene the 1 - 10 bond is comparable in length to both the 1 - 9 and 2 - 3 bonds, both of which were included in the NPSO wavefunction. Whereas, as already noted, in azulene the bridge bond is considerably longer than all other bonds;perhaps the non-inclusion is not such a drastic assumption.

This will be considered further, later.

V.ANTHRACENE AND PHENANTHRENE.

V.1:Introduction.

Pauncz (85) said: "contrasting the NPSO method with the AMO treatment, ... the former surpasses the latter when applied to small molecules." We chose to try to extend the NPSO method to larger systems - phenanthrene and anthracene - and to compare the NPSO results for these systems with those from an AMO treatment. Parker and Memory (79) have reported AMO calculations on these molecules, but only in an abstract. We have performed AMO calculations with the same integral values used in the NPSO calculations.

Extending the NPSO method in this manner tests the suggestion of Empedocles and Linnett further, (76).

V.2:The NPSO Wavefunction.

i)Anthracene:

The geometry and numbering of anthracene is shown in figure V-A. The numbering is after Amos and Snyder, (42); the geometry that of Cruickshank and Sparks, (80).

As previously the initial Slater determinant was built up from one-electron semi-localised orbitals centred on adjacent nuclei in the bonding region. The electrons were placed in these orbitals such that electrons in neighbouring orbitals had opposite spin. As with azulene, there are more bonds than pi-electrons and we had to decide which bonds to omit when forming the one-electron bonds.

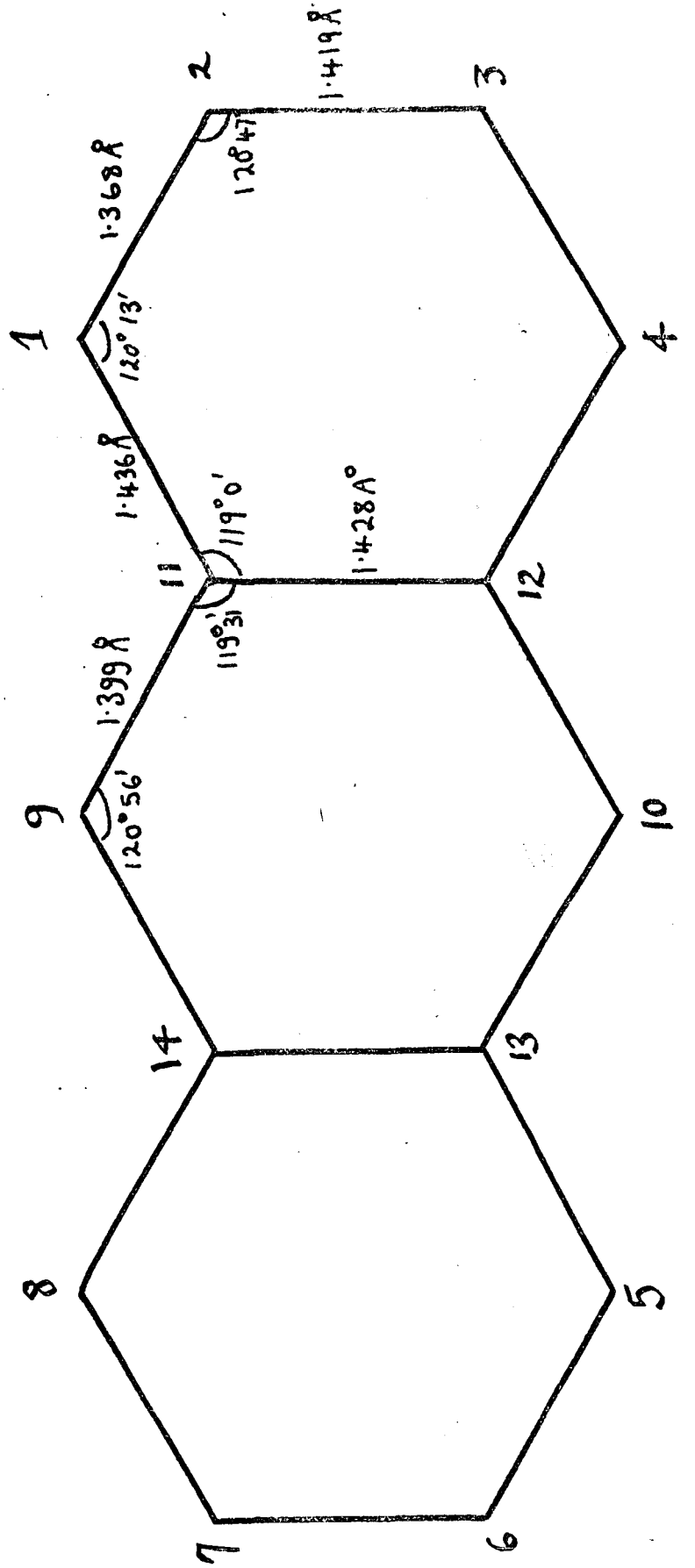
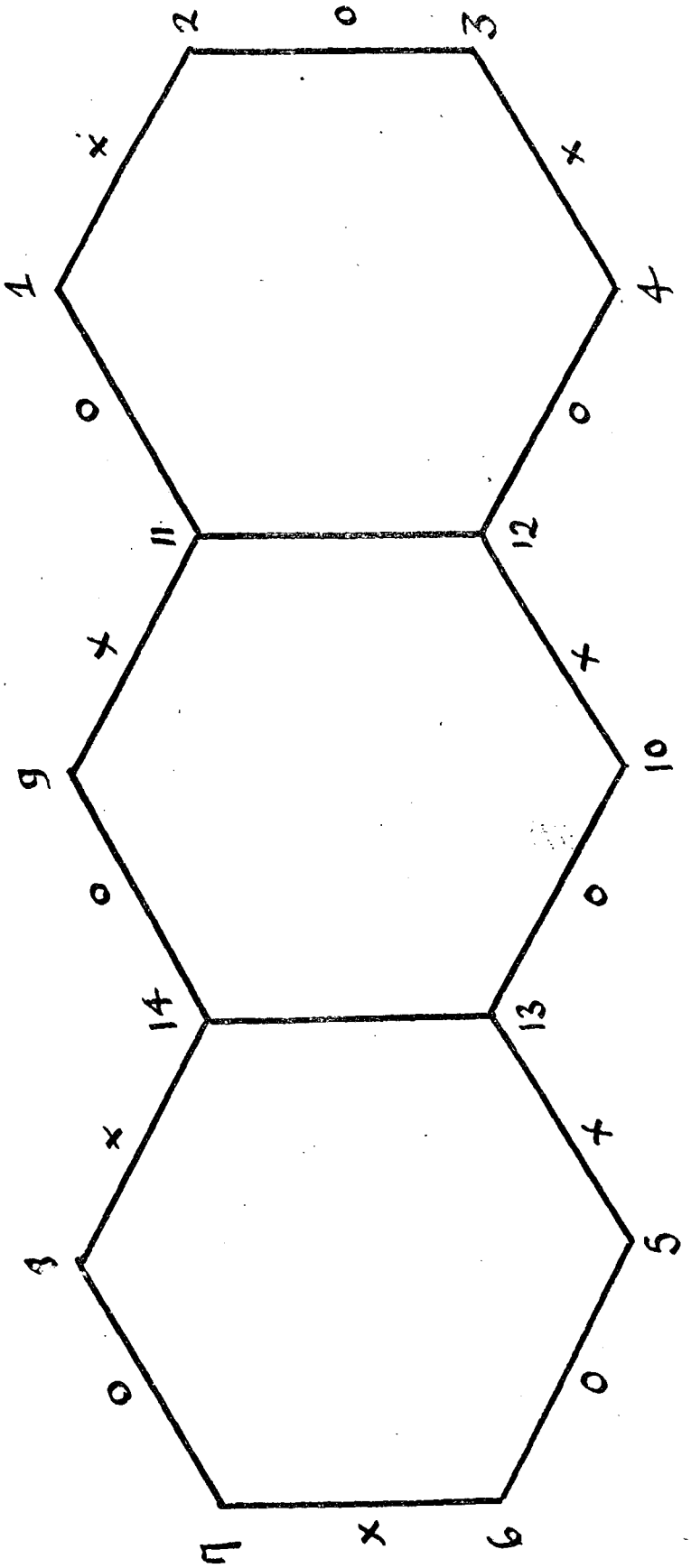


Figure V-A

The numbering and geometry of anthracene



x denotes an electron of α spin.

0 denotes an electron of β spin.

Figure V-B

The arrangement of α and β spin electrons in the one-electron orbitals, for anthracene

Despite the fact that the bridge bonds, (11 - 12) and (13 - 14) are only slightly longer than the (2 - 3) bond, they seemed the obvious candidates. Also, omitting them means that proper alternation of spins is possible. Thus the pi-electrons were distributed as in figure V-B, leading to a wavefunction of the form:-

$$\psi_1 = A\,|(\chi_1+k\chi_2)(1)\alpha(1)\ (\chi_3+k\chi_4)(2)\alpha(2)\ (\chi_{12}+k\chi_{10})(3)\alpha(2)\ (\chi_{13}+k\chi_5)(4)\alpha(4)\ (\chi_6+k\chi_7)(5)\alpha(5)\ (\chi_8+k\chi_{14})(6)\alpha(6)\ (\chi_9+k\chi_{11})(7)\alpha(7)\ (\chi_2+k\chi_3)(8)\beta(8)\ (\chi_4+k\chi_{12})(9)\beta(9)\ (\chi_{10}+k\chi_{13})(10)\beta(10)\ (\chi_5+k\chi_6)(11)\beta(11)\ (\chi_7+k\chi_8)(12)\beta(12)\ (\chi_{14}+k\chi_9)(13)\beta(13)\ (\chi_{11}+k\chi_1)(14)\beta(14)|$$

..5-1

The point group of anthracene is D_{2h}; the ground state belongs to the A_{1g} representation. Applying the correct symmetry projection operator to equation 5-1 gave the NPSO wavefunction as:-

$$\psi_T = \psi_I + \psi_{II} - \psi_{III} - \psi_{IV}$$

..5-2

where

ψ_{III} is obtained from ψ_I by interchanging α and β spins, and

ψ_{IV} is obtained from ψ_{II} by interchanging α and β spins,

and where $\psi_{II} = A|(\chi_4 + k\chi_3)(1)\alpha(1)\ (\chi_2 + k\chi_1)(2)\alpha(2)$
$(\chi_{11} + k\chi_9)(3)\alpha(3)\ (\chi_{12} + k\chi_8)(4)\alpha(4)$
$(\chi_7 + k\chi_6)(5)\alpha(5)\ (\chi_5 + k\chi_{13})(6)\alpha(6)$
$(\chi_{10} + k\chi_{12})(7)\alpha(7)\ (\chi_6 + k\chi_7)(8)\beta($
$(\chi_8 + k\chi_{14})(9)\beta(9)\ (\chi_9 + k\chi_{11})(10)\beta($
$(\chi_1 + k\chi_2)(11)\beta(11)\ (\chi_3 + k\chi_4)(12)\beta(12)$
$(\chi_{12} + k\chi_{10})(13)\beta(13)\ (\chi_{13} + k\chi_5)(14)\beta(14)$

..5-3

The wavefunction ψ_T is unchanged by replacing k with $1/k$.

To obtain the total wavefunction, with correct spin properties, a singlet projection operator was applied to equation 5-2, to give

$$\psi_S = O_0(\psi_I + \psi_{II}) \qquad ..5\text{-}4$$

Again, ψ_{III} and ψ_{IV} are included in ψ_S through the spin projection operator, O_0.

ii) Phenanthrene:

The geometry and numbering used for phenanthrene are given in figure V-C. The numbering scheme is, again, after Amos and Snyder, (42). The original intention was to use the experimental geometry, (81), but because of the large number of distinct internuclear distances computation of the integrals became an unwieldy task. Hence a regular geometry,

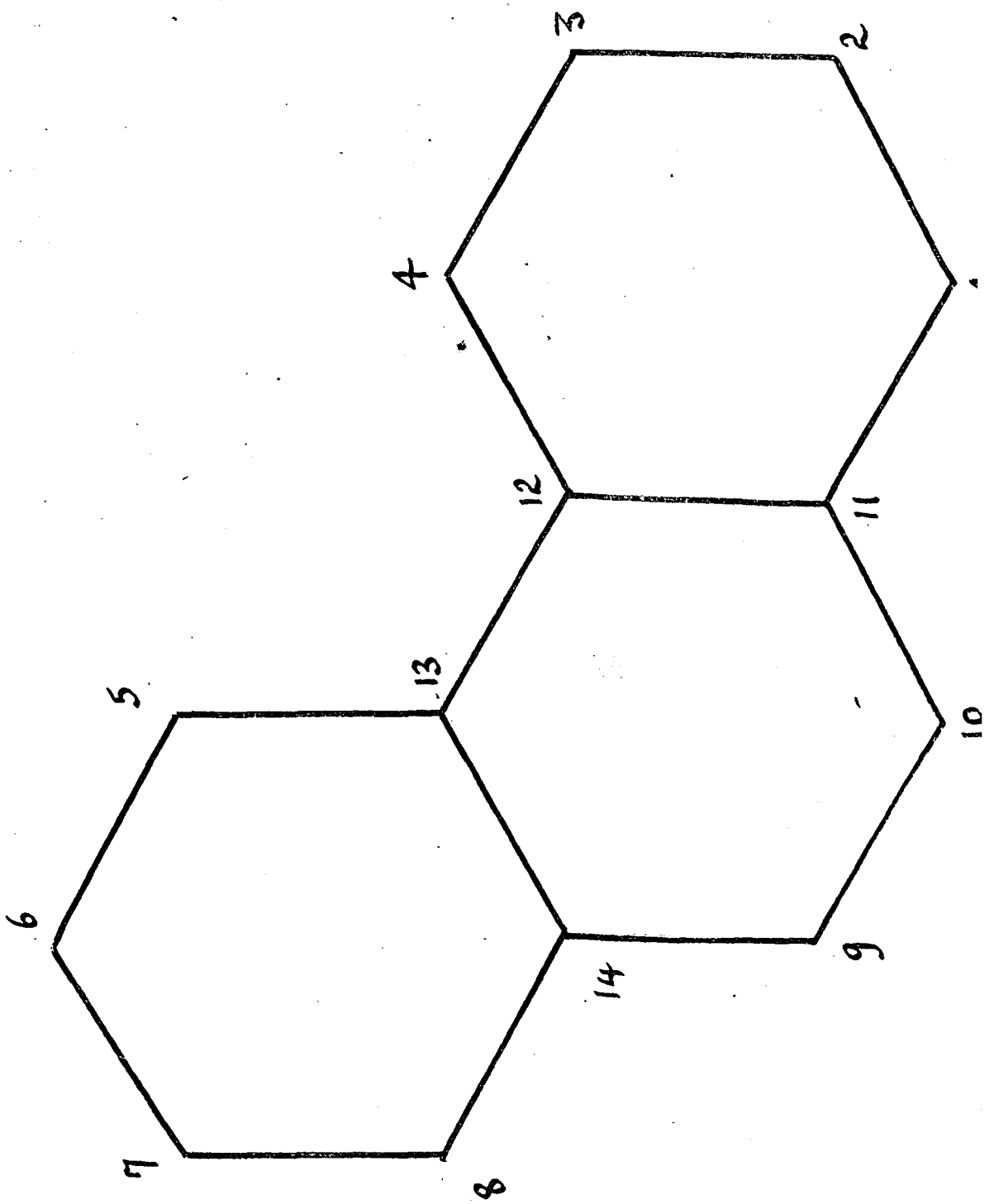


Figure V-C

The numbering scheme for phenanthrene.

of bond length 1.4 Å and bond angle 120°, was assumed.

The assumed geometry means that the bridge bonds, (13 -14) and (11 - 12) are the same length as all other bonds - but again we chose to omit these bonds when forming one-electron bonds. Hence, when distributing the pi-electrons, before setting up the initial Slater determinant, it is possible to alternate the spins such that each α electron is surrounded by electrons of β spin, and vice-versa; as in figure V-D.

The initial NPSO determinant was set up as

$$\psi_1 = A\Big|\begin{array}{cccc}(\chi_1+k\chi_{11})(1)\alpha(1) & (\chi_{10}+k\chi_9)(2)\alpha(2) & \cdots \\ (\chi_{14}+k\chi_8)(3)\alpha(3) & (\chi_7+k\chi_6)(4)\alpha(4) & \cdots \\ (\chi_5+k\chi_{13})(5)\alpha(5) & (\chi_{12}+k\chi_4)(6)\alpha(6) & \cdots \\ (\chi_3+k\chi_2)(7)\alpha(7) & (\chi_2+k\chi_1)(8)\beta(8) & \cdots \\ (\chi_{11}+k\chi_{10})(9)\beta(9) & (\chi_9+k\chi_{14})(10)\beta(10) & \cdots \\ (\chi_8+k\chi_7)(11)\beta(11) & (\chi_6+k\chi_5)(12)\beta(12) & \cdots \\ (\chi_{13}+k\chi_{12})(13)\beta(13) & (\chi_4+k\chi_3)(14)\beta(14) & \cdots \end{array}\Big| \quad \ldots 5\text{-}5$$

The point group of the phenanthrene molecule, with the assumed geometry, is C_{2v}; the ground state belongs to the A_1 representation.

Applying the symmetry projection operator gave the NPSO wavefunction as:

$$\psi_T = \psi_1 + \psi_{11} \quad \ldots 5\text{-}6$$

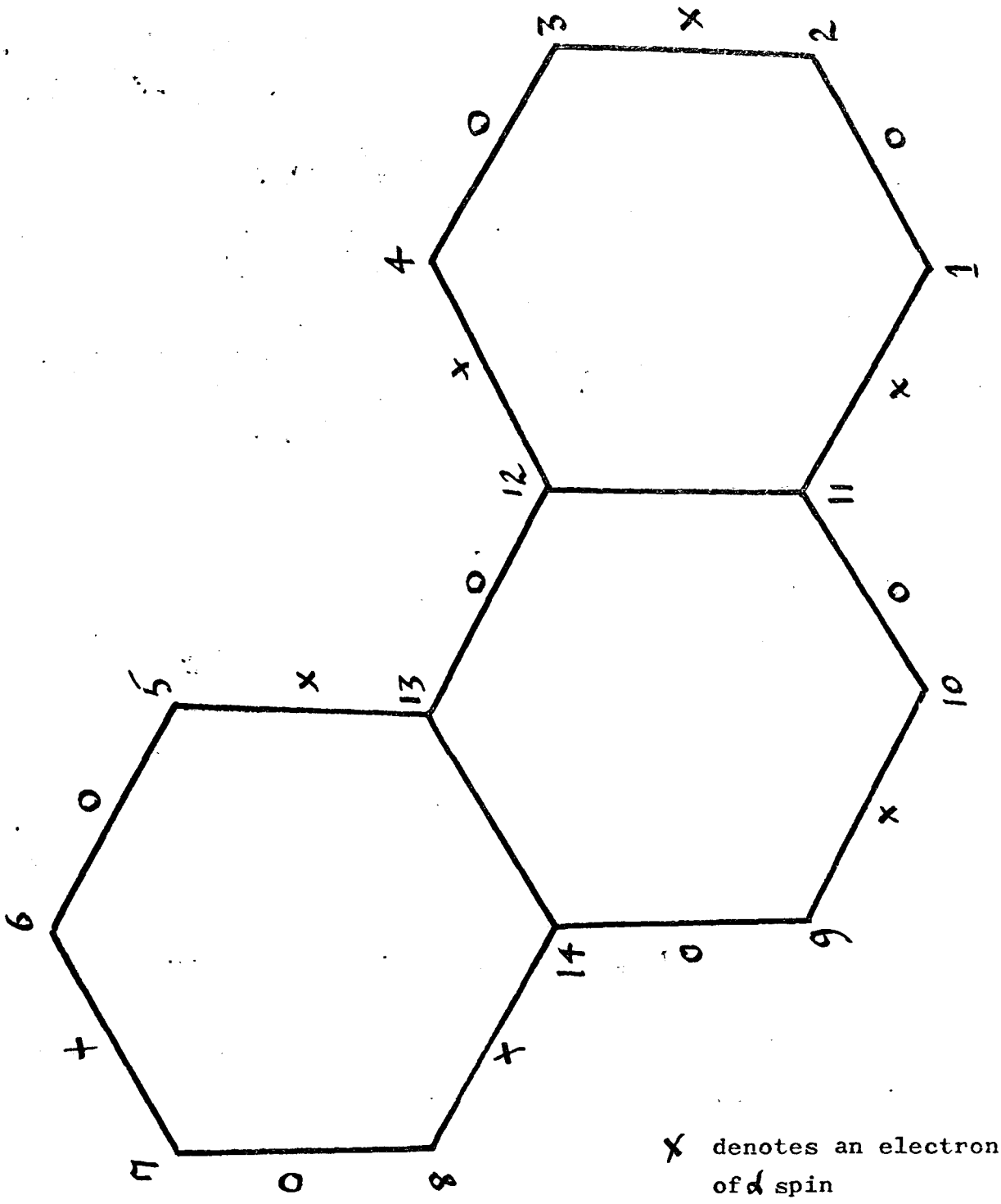


Figure V-D

The arrangement of α and β spin electrons in one-electron orbitals, for phenanthrene.

where $\psi_{II} = A|(k\chi_1 + \chi_{11})(1)\alpha(1)\ (k\chi_{10} + \chi_9)(2)\alpha(2)$
$(k\chi_{14} + \chi_8)(3)\alpha(3)\ (k\chi_7 + \chi_6)(4)\alpha(4)$
$(k\chi_5 + \chi_{13})(5)\alpha(5)\ (k\chi_{12} + \chi_4)(6)\alpha(6)$
$(k\chi_3 + \chi_2)(7)\alpha(7)\ (k\chi_2 + \chi_1)(8)\beta(8)$
$(k\chi_{11} + \chi_{10})(9)\beta(9)\ (k\chi_9 + \chi_{14})(10)\beta(10)$
$(k\chi_8 + \chi_7)(11)\beta(11)\ (k\chi_6 + \chi_5)(12)\beta(12)$
$(k\chi_{13} + \chi_{12})(13)\beta(13)\ (k\chi_4 + \chi_3)(14)\beta(14)$

..5-7

A pure singlet state is given by

$$\psi_0 = O_0(\psi_I + \psi_{II}) \qquad ..5\text{-}8$$

V.3:The Calculations.

i) Anthracene:

The integrals used were calculated so as to be analogous with those used previously. The one-electron integrals and coulomb integrals were calculated by the method of Ruedenberg, (82) - see Appendix I. All overlap integrals were included. Exact overlap integrals were used, but the orbital exponent used in these calculations was the value quoted by Ruedenberg. The Mulliken approximation,(83), was used for all the remaining two electron integrals. The integrals are given in table V-1.

Integral values for Anthracene, calculated using Ruedenberg's approximations.

element	coulomb integral	overlap integral	matrix elemen of the Hamiltonian
11	17.22703	1.0	-83.88960
22			-79.15477
99			-90.59952
11,11			-96.72070
12	9.18952	0.26030	-23.56937
13	5.65468	0.03483	-2.62129
14	4.91833	0.01481	-1.15044
15	2.50407	0.00001	-0.00109
16	2.20557	0.0	-0.00008
17	2.31714	0.0	-0.00030
18	2.87344	0.00009	-0.00715
19	5.54984	0.03132	-2.53826
1,10	3.76018	0.00176	-0.14230
1,11	8.85263	0.23232	-22.81618
1,12	5.56341	0.03176	-2.64880
1,13	3.32385	0.00051	-0.04245
1,14	3.75078	0.00172	-0.14301
23	8.93497	0.23908	-20.98533
26	1.92548	0.0	-0.0
27	1.96114	0.0	-0.0
29	3.79053	0.00189	-0.14874
2,10	3.35532	0.00056	-0.04426

Table V-1. .....continued.

Integral values for anthracene, continued.

element	coulomb integral	overlap integral	matrix elemen of Hamiltonia
2,11	5.63751	0.03424	-2.77210
2,12	4.92206	0.01488	-1.20505
2,13	2.80524	0.00007	-0.00543
2,14	2.91988	0.00011	-0.00907
9,10	4.94100	0.01529	-1.28839
9,11	9.03344	0.24723	-25.16755
9,12	5.61645	0.03352	-2.90761
11,12	8.89122	0.23548	-24.48094
11,13	4.91443	0.01473	-1.31220
11,14	5.63181	0.03404	-3.03288

Table V-1.

As previously, we calculated the molecular orbital energy, using the eigenvectors of the overlap matrix as initial MO's,(table V-2), and the SCF-LCAO-MO energy by Roothaan's method. The SCF-MO's are given in table V-4. We carried out NPSO calculations to the two degrees of approximation previously discussed. We calculated the unprojected NPSO energy and the projected and unprojected energy, (equation 3-52), since we have suggested that this energy is near to that obtainable from a fully spin projected wavefunction.

Since the only previously reported calculations within the AMO framework used different integrals, we performed a one parameter AMO calculation, using as starting orbitals both eigenvectors of the overlap matrix, and SCF-MO's. The results are given in table V-3. We tried to reproduce the results quoted by Parker and Memory, (79). They used an assumed geometry, bond lengths all 1.4 Å and angles 120°;they neglected all overlap integrals, except nearest neighbours, and also included only the Hamiltonian elements between neighbours. The integrals used are given in table V-5. With these approximations we also performed a MO calculation, using eigenvectors of the complete overlap matrix, (quoted in table V-2), as MO's, and an unprojected NPSO calculation, equation 3-49. The results are given in table V-6.

Eigenvectors of the overlap matrix, for Anthracene.

atom nos.	1,4,5 & 8.	2,3,6, & 7.	9,10	11,12, 13 & 14.	symmetry.
molecular orbital					
1	0.1688	0.1330	0.2320	0.2692	S_1S_2
2	-0.2366	-0.2530	0.0	-0.2023	S_1A_2
3	-0.1483	-0.3343	0.2335	0.1576	S_1S_2
4	-0.2479	-0.1093	0.3475	-0.2364	A_1S_2
5	-0.3728	-0.1998	0.0	-0.1725	A_1A_2
6	-0.0216	0.3016	0.0	-0.3520	S_1A_2
7	0.2958	0.2258	-0.4249	0.1023	A_1A_2

Table V-2.

Energy results for Anthracene.

all energies are quoted in e.V.

method	energy	k
MO (eigenvectors of the overlap matrix)	-776.3566 e.V.	
SCF-LCAO-MO	-777.2444 e.V.	
AMO (eigenvectors of the overlap matrix)	-776.9827 e.V.	λ= 0.927 [1]
AMO (SCF-MO)	-777.3830 e.V.	λ= 0.971
unprojected NPSO	-781.1359 e.V.	0.215
unprojected and projected NPSO	-782.0769 e.V.	0.2

[1] $\lambda = \cos 2\theta$

If k = 0.25 the following results are obtained:-

unprojected NPSO	-781.o380 e.V.
projected and unprojected NPSO	-781.8578 e.V.

Table V-3.

SCF - LCAO molecular orbitals for Anthracene.

atom nos..	1,4,5 & 8.	2,3,6 & 7.	9,10	11,12, 13, & 14	symmetry
molecular orbital					
1	0.1312	0.1004	0.2338	0.3034	S_1 S_2
2	0.2174	0.2378	0.0	0.2403	S_1 A_2
3	0.2237	0.1301	0.3253	0.2666	A_1 S_2
4	-0.1905	-0.3384	0.1585	0.1520	S_1 S_2
5	-0.0786	-0.2767	0.0	0.3685	S_1 A_2
6	-0.3563	-0.2358	0.0	-0.1638	A_1 A_2
7	0.2983	0.2384	-0.3926	-0.1302	A_1 S_2

Table V-4.

Integral values for anthracene,(Parker and Memory).

element	coulomb integral	overlap integral	matrix element of the Hamiltonian.
11	17.22703	1.0	-84.40063
22			-79.12024
33			-90.98039
11,11			-97.77918
12	9.02847	0.24682	-22.36429
13	5.56114	0.0	0.0
14	4.94787	0.0	-0.0
15	2.54484	0.0	-0.0
16	2.22656	0.0	-0.0
17	2.33896	0.0	-0.0
18	2.92895	0.0	-0.0
1,10	3.80018	0.0	-0.0
2,10	3.36759	0.0	-0.0
2,13	2.81686	0.0	-0.0
36	1.96697	0.0	-0.0
37	1.93193	0.0	-0.0
1,11	9.02847	0.24682	-24.43959
9,11	9.02847	0.24682	-25.25160
11,12	9.02847	0.24682	-25.86323
23	9.02847	0.24682	-21.71264

Table V-5

Energy results for anthracene, (Parker and Memory data).

all energies are quoted in e.V.

method	energy	k
MO	-778.7144 e.V.	
AMO	-778.7913 e.v.	λ = 0.979
unprojected NPSO	-784.4300 e.v.	0.2075

Table V-6.

ii)Phenanthrene:

Again the integrals were calculated using Ruedenberg's methods and the Mulliken approximation. The integrals are quoted in table V-7.

Calculations corresponding to those for anthracene were performed. The results are given in tables V-8 to V-10. Again we tried to reproduce Parker and Memory's results - this time with more success. The results are given in table V-12, with those obtained from a MO energy calculation and an unprojected NPSO calculation. The integrals used are given in table V-11.

V.4: Discussion.

For both phenanthrene and anthracene the one parameter AMO method lowers the energy from the MO energy by only a small amount - less than an electron volt, (e.V.), in each case. Using the SCF-MO's as starting orbitals worsens the situation - here the energy lowering is less than 0.24 e.V.. Two possible reasons for this have been suggested,(84).

A single parameter may be too restrictive; but a seven parameter method would be difficult to perform.

Also, it may be necessary to perform unitary transformations amongst the anti-bonding orbitals before forming the AMO's. Pauncz has discussed at some length, (67), the choice of starting orbitals and he stated that the best criterion for the choice of molecular orbitals "should be decided soley on the basis of the final AMO calculation;

Integral values for Phenanthrene, (Ruedenberg).

element	coulomb integral	overlap integral	matrix elemen of the Hamiltonian.
11	17.22703	1.0	-84.40063
22			-79.96897
33			-81.13376
44			-88.42458
99			-87.27489
11,11			-97.77918
12,12			-101.48468
12	9.02847	0.24682	-22.46904
13	5.65114	0.03470	-2.65698
14	4.94987	0.01545	-1.23935
15	2.92895	0.00012	-0.00938
16	2.33896	0.00001	-0.00038
17	2.22656	0.0	-0.00015
18	2.54484	0.00002	-0.00133
19	3.80018	0.00194	-0.15425
1,14	3.36759	0.00059	-0.04912
25	2.81686	0.00007	-0.00554
27	2.04316	0.0	-0.0
23			-22.06587
34			-23.10938
4,12			-25.39348
12,13			-26.77782
12,11			-26.32052
10,11			-24.79430

.....continued

Table V-7.

Integral values for phenanthrene, continued.

element	coulomb integral	overlap integral	matrix element of Hamiltonian
10,9			-23.72538
1,11			-24.43959
1,10			-2.76354
1,12			-2.97813
1,13			-0.16622
24			-2.70659
26			-0.00015
29			-0.00906
2,10			-0.14996
2,11			-2.83693
2,12			-1.29178
2,13			-0.04891
2,14			-0.00580
35			-0.04597
36			0.00127
39			-0.00554
3,10			-0.04563
3,11			-1.27215
3,12			-2.92144
3,13			-0.16306
3,14			-0.00963
45			-1.27044
49			-0.04776
4,10			-0.15814
4,11			-2.98366

.....continued

Table V-7.

Integral values for phenanthrene, continued.

element	coulomb integral	overlap integral	matrix element of Hamiltonian
4,13			-3.04795
4,14			-0.16653
9,11			-2.96371
9,12			-1.34822
9,13			-3.02800
11,13			-3.17830
11,14			-1.38651

Table V-7.

Eigenvectors of the overlap matrix for phenanthrene

atom nos. / molecular orbital	1 ± 8	2 ± 7	3 ± 6	4 ± 5	9 ± 10	11 ± 14	12 ± 13	symmetry (s or a
1	0.1629	0.1250	0.1301	0.1825	0.1925	0.2626	0.2973	s
2	-0.2637	-0.2643	-0.2449	-0.2019	0.0796	-0.2378	-0.1464	a
3	-0.0067	-0.1955	-0.2836	-0.2391	0.3834	0.1918	-0.0608	s
4	-0.2996	-0.3405	-0.1354	0.1761	-0.0957	-0.0354	0.3517	s
5	-0.2348	0.0996	0.3401	0.2700	0.1741	-0.3511	-0.0331	a
6	0.2327	0.3752	0.0313	-0.3436	0.1122	-0.2004	-0.2884	a
7	0.3200	0.0265	-0.3142	-0.2085	-0.3943	0.1625	0.1908	s

Table V-8

SCF-LCAO molecular orbitals for phenanthrene.

atom no.	1 ± 8	2 ± 7	3 ± 6	4 ± 5	9 ± 10	11 ± 14	12 ± 13	symmetry (s or a)
molecular orbital								
1	0.1653	0.1321	0.1327	0.1613	0.1368	0.2900	0.3124	s
2	0.2385	0.2337	0.2096	0.1874	-0.0681	0.3078	0.1953	a
3	0.0021	-0.2007	-0.3080	-0.2197	0.3509	0.2356	-0.0502	s
4	-0.2706	-0.3371	-0.1361	0.1297	-0.1517	-0.0314	0.3800	s
5	0.1281	-0.1750	-0.3630	-0.2473	-0.1049	0.3930	0.0886	a
6	0.3050	0.3441	-0.0084	-0.3380	0.0442	-0.0998	-0.3367	a
7	0.3057	0.0642	-0.2684	-0.2427	-0.4338	0.1760	0.1228	s

Table V-9.

Energy results for Phenanthrene, (Ruedenberg data).

all energies quoted in e.V.

method	energy	k
MO (eigenvectors of overlap matrix)	-787.2687 e.V.	
SCF - LCAO -MO	-788.2206 e.V.	
AMO (eigenvectors of overlap matrix)	-788.0756 e.V.	λ = 0.92
AMO (SCF - MO)	-788.2891 e.V.	λ = 0.98
unprojected NPSO	-792.1193 e.V.	0.2148
projected and unprojected NPSO	-793.0594 e.V.	0.2

If k = 0.25 the following results are obtained:-

unprojected NPSO	-792.0214 e.V.
projected and unprojected NPSO	-792.8408 e.V.

Table V-10

Integral values for phenanthrene,(Parker and Memory).

element	coulomb integral	overlap integral	matrix element of the Hamiltonian.
11	17.22703	1.0	-84.40063
22			-79.96897
33			-81.13376
44			-88.42458
99			-87.27489
11,11			-97.77918
12,12			-101.48468
12	9.02847	0.24682	-22.46904
23	9.02847	0.24682	-22.06587
34	9.02847	0.24682	-23.10938
4,12	9.02847	0.24682	-25.39348
11,12	9.02847	0.24682	-26.32052
12,13	9.02847	0.24682	-26.77782
10,11	9.02847	0.24682	-24.79430
10,9	9.02847	0.24682	-23.72538
1,11	9.02847	0.24682	-24.43959

Table V-11.

Energy results for phenanthrene,(Parker and Memory data).

all results are quoted in e.V.

method	energy	k
MO	-786.0876 e.V.	
AMO	-791.7803 e.V.	λ = 0.682
unprojected NPSO	-791.3210 e.V.	0.208

Table V-12.

the lower the final minimum, the better the choice of molecular orbitals."

For both molecules the two NPSO wavefunctions give good energy lowerings, and, as expected, that of the projected and unprojected wavefunction is the larger. Here, perhaps, non-inclusion of the bridge bonds - although comparable in length to the other bonds in the molecules - is not so critical as is the choice of molecular orbitals for the AMO method.

Both sets of calculations support Empedocles and Linnett's suggestion (76), since the minima are very close to k = 0.25.

The results of the calculations using Parker and Memory's approximations appear to conflict. We were not able to reproduce Parker and Memory's results for anthracene. They quoted a lowering of 5.85 e.V. with a variable parameter, λ, equal to 0.676; whereas we obtained a lowering of less than 1.0 e.V. with a mixing parameter of $\lambda = 0.979$. For phenanthrene we did reproduce Parker and Memory's results. For both anthracene and phenanthrene the unprojected NPSO wavefunction gives an energy minimum at $k \simeq 0.208$, and an energy lowering of about 5.5 e.V. For anthracene this is considerably greater than the AMO lowering we obtained, (but not Parker and Memory's); whereas for phenanthrene the AMO energy is slightly lower. Since the relative performances of the NPSO method and AMO method, for phenanthrene varies, depending on the integral

approximations used, this would suggest that either, or both, of the methods may be sensitive to the integral approximations used. We shall go on to consider this further - for the benzyl radical.

VI.THE BENZYL RADICAL.

VI.1:Introduction.

The benzyl radical is to the theory of neutral hydrocarbon radicals, as benzene is to that of conjugated hydrocarbons. Since it is relatively easy to produce, (86), it has been well studied experimentally, (87). Being an alternant hydrocarbon, simple as well as more sophisticated theories have been applied to it. The electronic structure of the benzyl radical has been studied, amongst many methods, by the valence bond, VB, method, (87),(88), the Huckel molecular orbital, HMO, method, (87), the UHF method, (89),(42) and the SCF-MO-CI method, (90),(87),(91). Here the NPSO method and the AMO method are applied to it.

The radical was assumed to have a regular geometry of bond length 1.4 Å and bond angle 120^{o}. The numbering,that of Amos and Snyder,(42), is shown in figure VI-A.

VI.2: The NPSO Wavefunction.

Here there is some complication; for there will always be two electrons of the same spin in adjacent semi-localised one-electron orbitals.

See, for example figures VI-B, VI-C,VI-D.

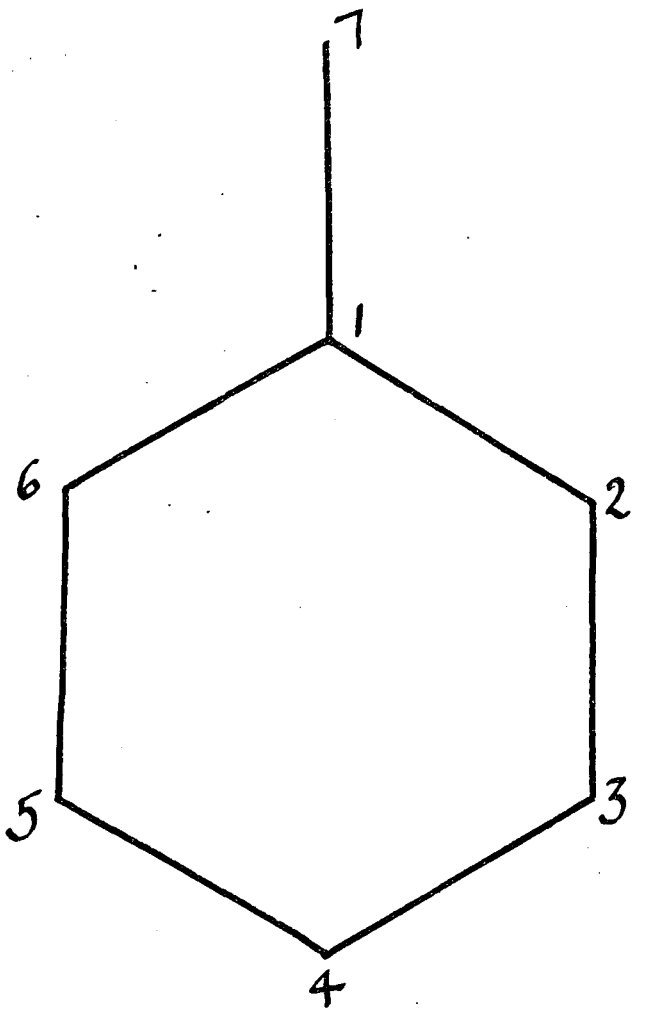
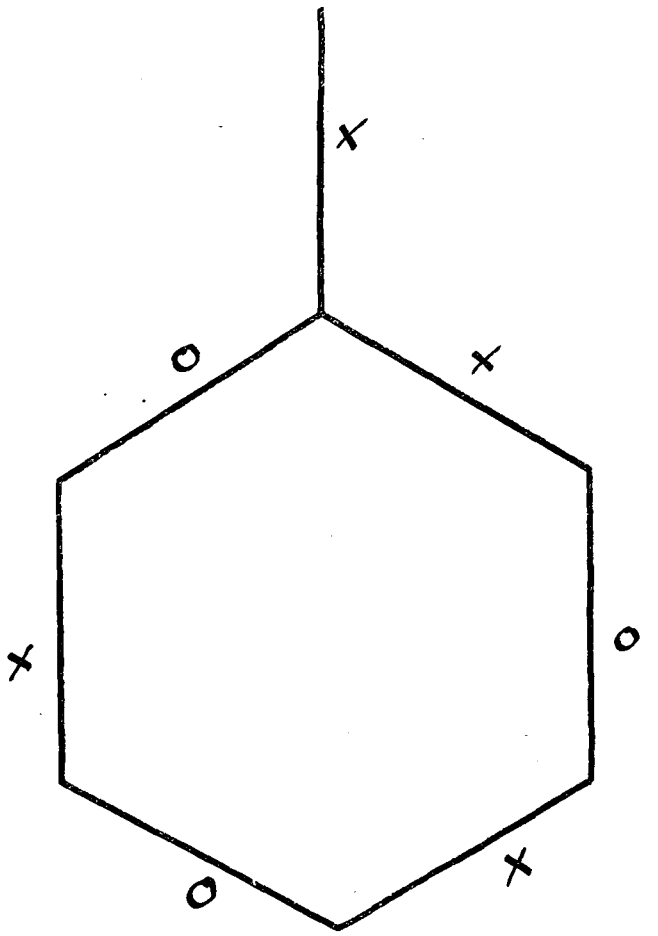


Figure VI-A

The numbering of atoms for the benzyl radical.

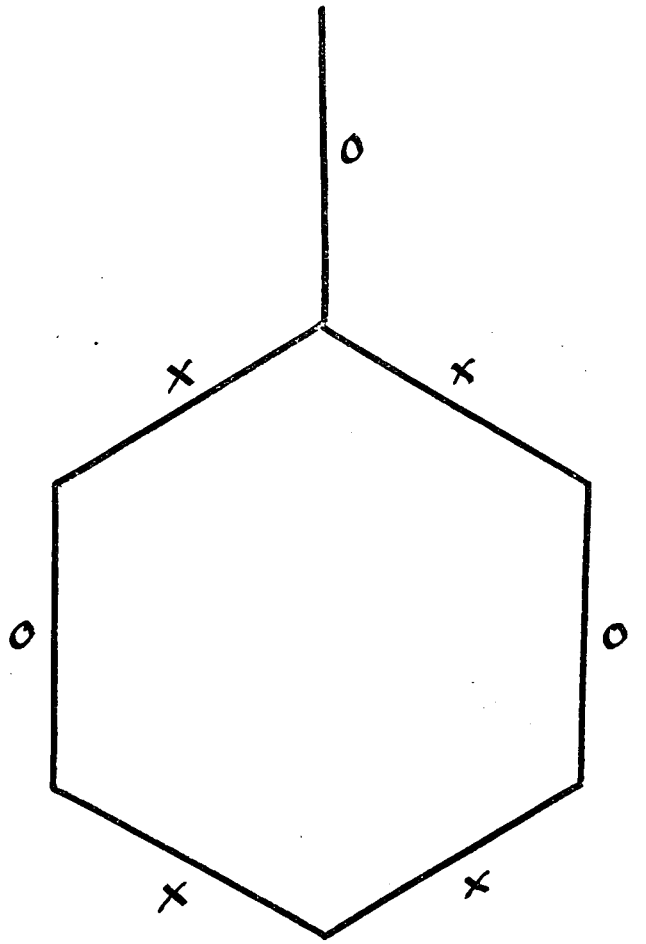


X denotes α spin electron

O denotes β spin electron

Figure VI-B

The electron spin arrangement for the Benzyl radical

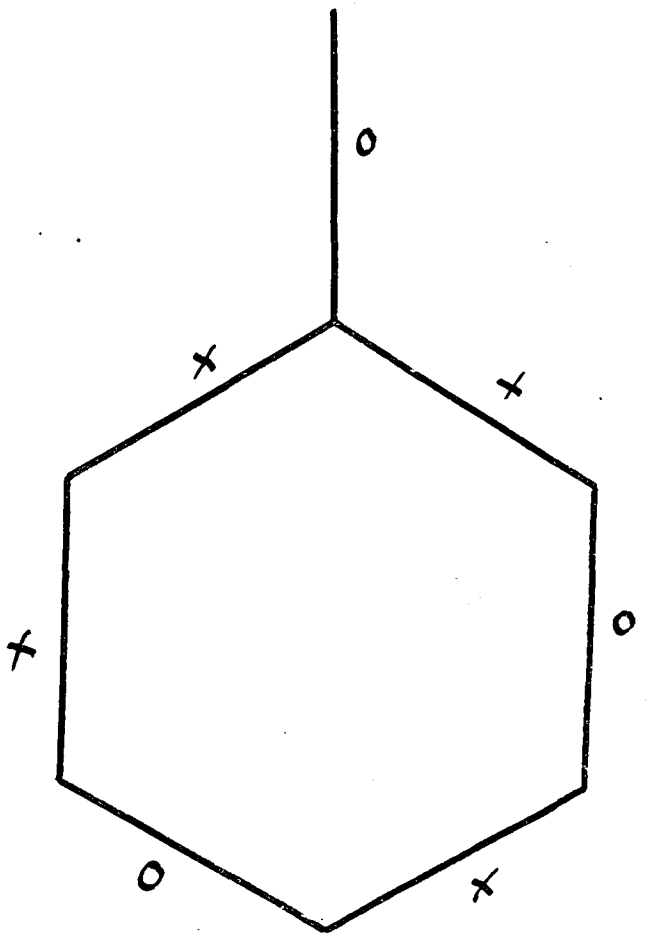


× denotes α spin electron

O denotes β spin electron

Figure VI-C

the electron spin arrangement for the Benzyl radical



X denotes spin electron

O denotes spin electron

Figure VI-D

the electron spin arrangement for the Benzyl radical

There are also two possible ways of constructing the initial NPSO Slater determinant.

$$\psi_I(A) = A \left| \begin{array}{ll} (\chi_1 + k\chi_2)(1)\,\alpha(1) & (\chi_3 + k\chi_4)(2)\,\alpha(2) \\ (\chi_5 + k\chi_6)(3)\,\alpha(3) & (\chi_1 + k\chi_7)(4)\,\alpha(4) \\ (\chi_2 + k\chi_3)(5)\,\beta(5) & (\chi_4 + k\chi_5)(6)\,\beta(6) \\ (\chi_6 + k\chi_1)(7)\,\beta(7) & \end{array} \right| \qquad ..6\text{-}1$$

or

$$\psi_I(B) = A \left| \begin{array}{ll} (\chi_1 + k\chi_2)(1)\,\alpha(1) & (\chi_3 + k\chi_4)(2)\,\alpha(2) \\ (\chi_5 + k\chi_6)(3)\,\alpha(3) & (\chi_7 + k\chi_1)(4)\,\alpha(4) \\ (\chi_2 + k\chi_3)(5)\,\beta(5) & (\chi_4 + k\chi_5)(6)\,\beta(6) \\ (\chi_6 + k\chi_1)(7)\,\beta(7) & \end{array} \right| \qquad ..6\text{-}2$$

To both we must apply a symmetry projection operator. The benzyl radical has point group C_{2v}, and a doublet ground state belonging to the B_2 representation. Thus

$$\psi_T(A) = \psi_I(A) + \psi_{II}(A) \qquad ..6\text{-}3$$

and

$$\psi_T(B) = \psi_I(B) + \psi_{II}(B) \qquad ..6\text{-}4$$

where

$$\psi_{II}(A) = A\,|\,(\chi_1+k\chi_6)(1)\alpha(1)\;\;(\chi_5+k\chi_4)(2)\alpha(2)\;\;(\chi_3+k\chi_2)(3)\alpha(3)\;\;(\chi_1+k\chi_7)(4)\alpha(4)\;\;(\chi_2+k\chi_1)(5)\beta(5)\;\;(\chi_4+k\chi_3)(6)\beta(6)\;\;(\chi_6+k\chi_5)(7)\beta(7)\,| \qquad ..6\text{-}5$$

and

$$\psi_{II}(B) = A\,|\,(\chi_1+k\chi_6)(1)\alpha(1)\;\;(\chi_5+k\chi_4)(2)\alpha(2)\;\;(\chi_3+k\chi_2)(3)\alpha(3)\;\;(\chi_1+k\chi_1)(4)\alpha(4)\;\;(\chi_2+k\chi_1)(5)\beta(5)\;\;(\chi_4+k\chi_3)(6)\beta(6)\;\;(\chi_6+k\chi_5)(7)\beta(7)\,| \qquad ..6\text{-}6$$

The final NPSO wavefunctions, with correct spin and symmetry properties, can be obtained from equations 6-3 and 6-4, by the application of a doublet spin projection operator; to give

$$\psi_A = O_D\,(\psi_I(A) + \psi_{II}(A)) \qquad ..6\text{-}7$$

and

$$\psi_B = O_D\,(\psi_I(B) + \psi_{II}(B)) \qquad ..6\text{-}8$$

VI.3: Calculations.

Methods of calculation

i) The NPSO method.

As previously the various NPSO wavefunctions were used as approximations to the fully spin projected

wavefunction,(equations 6-7 and 6-8). Both equations 6-3 and 6-4 were used to perform unprojected NPSO energy calculations. Here the total energy, E, was calculated using, for wavefunction ψ_A ,

$$E = \frac{\langle \psi_i(A)|H|\psi_i(A)\rangle + \langle \psi_i(A)|H|\psi_{ii}(A)\rangle}{\langle \psi_i(A)|\psi_i(A)\rangle + \langle \psi_i(A)|\psi_{ii}(A)\rangle} \qquad ..6\text{-}9$$

and the comparable equation for the wavefunction ψ_B .

We also performed calculations analogous to those previously mentioned - and named annihilated NPSO, projected and unprojected NPSO and projected and annihilated NPSO methods.

However the benzyl radical is an open shell system; thus it is necessary to use the Harris formulae,(68), for calculation of the energy for a projected single Slater determinant.

$$E(1) = (n!)^{-1} \sum_{\ell=1}^{n} \sum_{k} (-1)^k C_k \Delta_\ell^k \langle \ell|h|\ell\rangle$$
$$+ (n!)^{-1} \sum_{\ell=1}^{n_\beta} \sum_{k} (-1)^{k+1} C_{k+1} \Delta_\ell^k \qquad ..6\text{-}10$$
$$[\lambda_\ell^* \langle \ell|h|\ell'\rangle + \lambda_\ell \langle \ell'|h|\ell\rangle]$$
$$(n_\alpha \geq n_\beta)$$

where

$E(1)$ denotes the expectation value of the one-electron part of the Hamiltonian,

$$C_k = \frac{4S+2}{2S+n+2} \sum_{j=0}^{S-M_S} (-1)^{S-M_S+k-j} \times \qquad ..6\text{-}11$$
$$\left[\binom{S-M_S}{j} \binom{S+M_S}{S-M_S-j} \binom{\frac{n}{2}+S}{n_\alpha+j-k}^{-1} \right]$$

and Δ^k is $\sum_i \prod_i |\lambda_i|^2$

where the sum is over all i, with k interchanges; and the subscript (ℓ) in Δ^k_ℓ denotes that the only interchanges involved are not those containing the electron ℓ.

The expectation value of the two-electron part of the Hamiltonian is given by

$$E(2) = \sum_{m=2}^{n_\alpha}\sum_{\ell=1}^{m-1} D^0_{\ell m}[\langle \ell m|h|\ell m\rangle - \langle \ell m|h|m\ell\rangle] \qquad ..6\text{-}12$$

$$+ \sum_{m=2}^{n_\beta}\sum_{\ell=1}^{m-1} D^0_{\ell m}[\langle \ell' m'|h|\ell' m'\rangle - \langle \ell' m'|h|m'\ell\rangle]$$

$$+ \sum_{\ell=1}^{n_\alpha}\sum_{m=1}^{n_\beta} [D^0_{\ell m}\langle \ell m'|h|\ell m\rangle + D'_{\ell m}\langle \ell m'|h|m'\ell\rangle$$

$$+ \sum_{\ell=1}^{n}\sum_{m=1}^{n_\beta} 2\times D'_{\ell m}[\lambda_m(\langle \ell m|h|\ell m'\rangle - \langle \ell m|h|m'\ell\rangle]$$

$$+ \sum_{m=2}^{n_\beta}\sum_{\ell=1}^{m-1} 2[D^2_{\ell m}\lambda_\ell\lambda_m(\langle \ell m|h|\ell' m'\rangle - \langle \ell m|h|m'\ell'\rangle)$$

$$+ \lambda_\ell\lambda_m(D^2_{\ell m}\langle \ell' m|h|\ell m'\rangle + D'_{\ell m}\langle \ell' m|h|m'\ell\rangle)$$

(Orbitals ℓ and ℓ' are paired, as are m and m'.)

where

$$D^0_{\ell m} = (n!)^{-1}\sum_k (-1)^k C_k \Delta^k_{\ell m}$$

$$D'_{\ell m} = (n!)^{-1}\sum_k (-1)^{k+1} C_{k+1} \Delta^k_{\ell m} \qquad ..6\text{-}13$$

$$D^2_{\ell m} = (n!)^{-1}\sum_k (-1)^{k+2} C_{k+2} \Delta'_{\ell m}.$$

ii) The MO method.

As previously we calculated the LCAO-MO energy, for reference, using the eigenvectors of the overlap matrix as molecular orbitals. The MO energy of an open shell system is given by

(using previous notation)

$$E = \sum_{i=1}^{n} I_{ii} + \sum_{i=j}^{n} (ii|jj) - \sum_{i<j}^{\alpha} (ij|ji) - \sum_{i<j}^{\beta} (ij|ji) \qquad ..6\text{-}14$$

iii) The SCF-MO method.

There are two possible methods of calculating an LCAO-SCF-MO energy. Both the RHF method of Roothaan, (equation 2-15) and the UHF method of Polpe and Nesbet (equations 2-18 to 2-23) were used.

iv) the AMO method.

The only previously reported calculation on the benzyl radical, using the AMO method is that of Vincow and Johnson, (92). Here the best wavefunction was obtained by criteria other than energy minimisation.

Thus a one parameter AMO calculation, using eigenvectors of the overlap matrix as initial MO's, was performed. The AMO's were set up as

$$u_i \ (i=1,3) = \cos\theta\,\psi_i + \sin\theta\,\psi_{8-i}$$

$$v_i \ (i=5,7) = \cos\theta\,\psi_i - \sin\theta\,\psi_{8-i} \qquad ..6\text{-}15$$

where u_i and v_i are the AMO's containing, respectively, α and β electrons;
ψ_i denotes the initial molecular orbitals,
and θ is a variable parameter.
u_i, if i = 4, was equal to the non-bonding MO; thus

$$u_4 = \psi_4 \qquad ..6\text{-}16$$

Application of a doublet spin projection operator to the determinant

$$\psi = A|u_1 u_2 u_3 u_4 v_1 v_2 v_3| \qquad ..6\text{-}17$$

gave a suitable wavefunction, such that it was possible to use equations 6-10and 6-12 to calculate the AMO energy.

Initially the same integral approximations were used in this work as previously - see appendix I. The one-electron, two centre and overlap integrals were calculated by Ruedenberg's method. The Mulliken approximation was used for the remaining two electron integrals. The values are listed in table VI-1.

VI.4: Results and Discussion.

Table VI-2 contains the eigenvectors of the complete overlap matrix. Tables VI-4 and VI-3, respectively, contain the UHF and RHF LCAO-SCF-MO's for the integral approximation "Ruedenberg core, Mulliken approximation". Although the RHF and UHF SCF-MO energies were

Integral values for the Benzyl radical,(Ruedenberg).

element	coulomb integral	overlap integral	matrix element of the Hamiltonian.
11	17.22703	1.0	-70.47628
22	17.22703	1.0	-64.63525
33	17.22703	1.0	-62.78366
44	17.22703	1.0	-62.35171
77	17.22703	1.0	-53.50875
12	9.02847	0.24682	-18.24818
13	5.65114	0.03470	-2.01110
14	4.94988	0.01545	-0.89211
37	3.79954	0.00193	-0.10043
47	3.36759	0.00059	-0.03026
17			-17.17910
23			-17.60287
24			-1.94500
25			-0.86935
26			-1.98463
27			-1.83431
34			-17.32106
35			-1.92037
36			-0.86935

Table VI-1.

Eigenvectors of the overlap matrix for the benzyl radical.

atom nos.	1	2 ± 6	3 ± 5	4	7	symmetry (s or a)
molecular orbital						
1	0.3756	0.3188	0.2872	0.2778	0.1892	s
2	-0.4348	-0.1046	0.3008	0.4765	-0.4016	s
3	0.0	-0.4571	-0.4571	0.0	0.0	a
4	-0.0454	-0.3901	0.0138	0.4102	0.7599	s
5	0.0	0.5836	0.5836	0.0	0.0	a
6	-0.6208	0.1333	0.4357	-0.6785	0.4503	s
7	-0.7017	0.5519	-0.4725	0.4504	0.2989	s

Table VI-2.

RHF - SCF - LCAO molecular orbitals.

atom nos.	1	2 ± 6	3 ± 5	4	7	symmetry (s or a)
molecular orbital.						
1	0.4681	0.3134	0.2791	0.2637	0.0147	s
2	0.5537	0.1437	-0.3172	-0.5293	0.0306	s
3	0.0	0.4377	0.4760	0.0	0.0	a
4	-0.0786	0.2547	0.0015	-0.1745	-0.9226	s
5	0.6692	-0.3685	-0.2855	0.6333	-0.4182	s
6	0.0	-0.5983	0.5683	0.0	0.0	a
7	-0.4782	0.5173	-0.5711	0.5954	0.1985	s

Table VI-3.

UHF - SCF - LCAO molecular orbitals.

atom nos.	1	2 ± 6	3 ± 5	4	7	symmetry (a or s)
molecular orbital						
1	0.0881	0.2247	0.1347	0.8096	0.0512	s
2	-0.2662	-0.5227	0.0022	0.4569	-0.1536	s
3	0.0	0.6869	0.1060	0.0	0.0	a
4	-0.2466	0.2734	0.0375	-0.0771	-0.8746	s
5	0.9529	0.0430	-0.1414	-0.0404	-0.0487	s
6	0.0	-0.0966	-0.6904	0.0	0.0	a
7	-0.1153	-0.0766	-0.6128	-0.1644	-0.0089	s

Table VI-4.

as expected, see table VI-5, the UHF orbitals seem unreasonable. This will be discussed further, later.

From table VI-5 it can be seen that the wavefunction NPSO-A gives consistently better results than those of NPSO-B. By considering the physical interpretation of the two wavefunctions this can be explained. From graphs VI-1 and VI-2, both annihilated NPSO energy plotted against k, for respectively, NPSO-A and NPSO-B wavefunctions, it is obvious that, unlike previously considered hydrocarbons, the wavefunction containing k as a variable parameter, is not equivalent to that containing $1/k$. Thus for each wavefunction there are two minima. A physical representation of both minima can be given.

Physical interpretations of the NPSO wavefunctions.

i) Wavefunction NPSO-A:

$$\psi_1(A) = A \left| \begin{array}{cc} (\chi_1 + k\chi_2)\alpha & (\chi_3 + k\chi_4)\alpha \\ (\chi_5 + k\chi_6)\alpha & (\chi_1 + k\chi_7)\alpha \\ (\chi_2 + k\chi_3)\beta & (\chi_4 + k\chi_5)\beta \\ (\chi_6 + k\chi_1)\beta & \end{array} \right| \quad \text{..6-1}$$

If k is less than 1.0, the wavefunction can be represented as in figure VI-E.

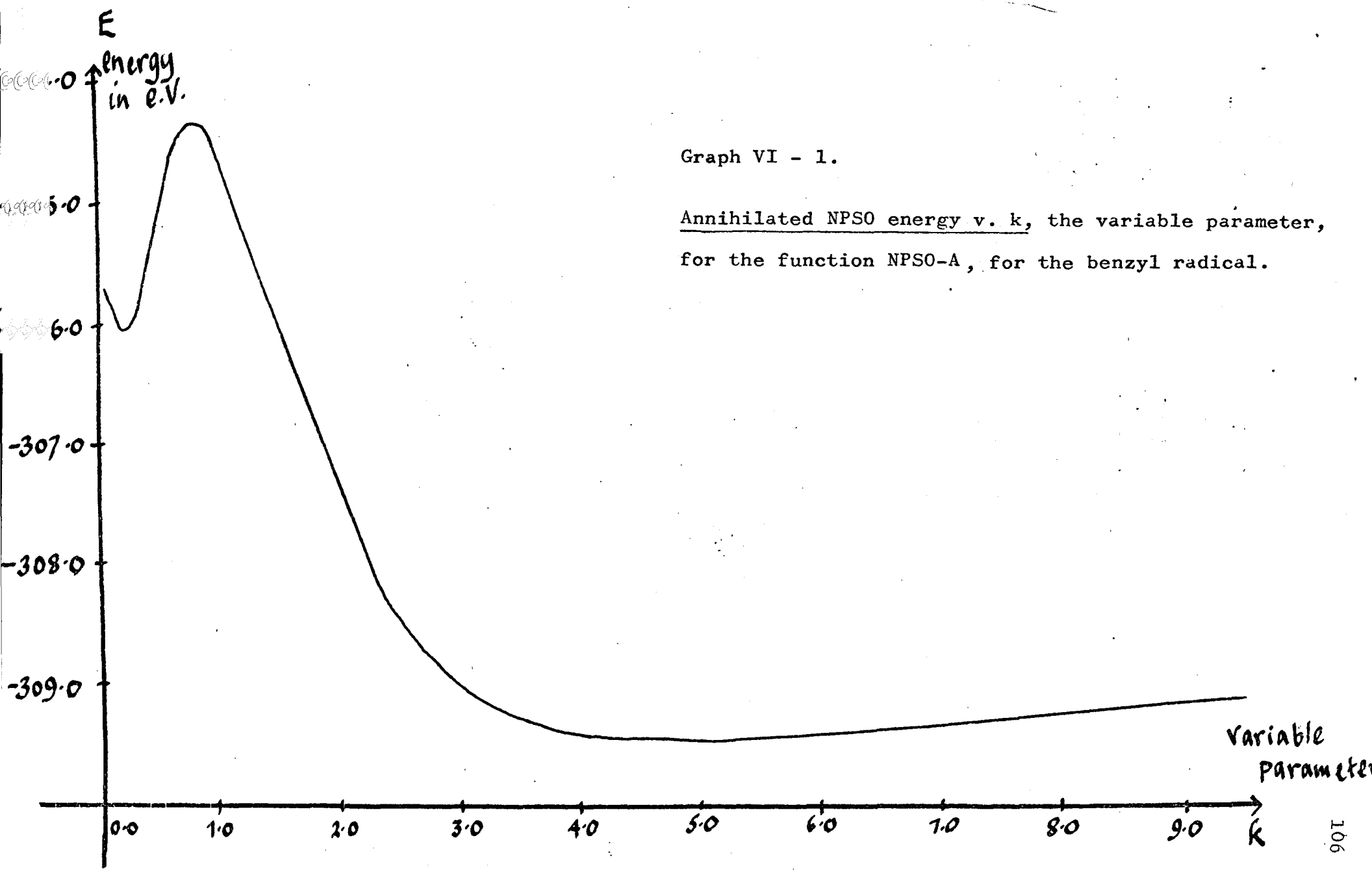
Here the semi-localised one-electron bonds containing α electrons will be displaced towards atoms 1,3,5, such that at atom 1, two one-electron

Energy results for the Benzyl radical,(Ruedenberg data).

all energies quoted in e.V.

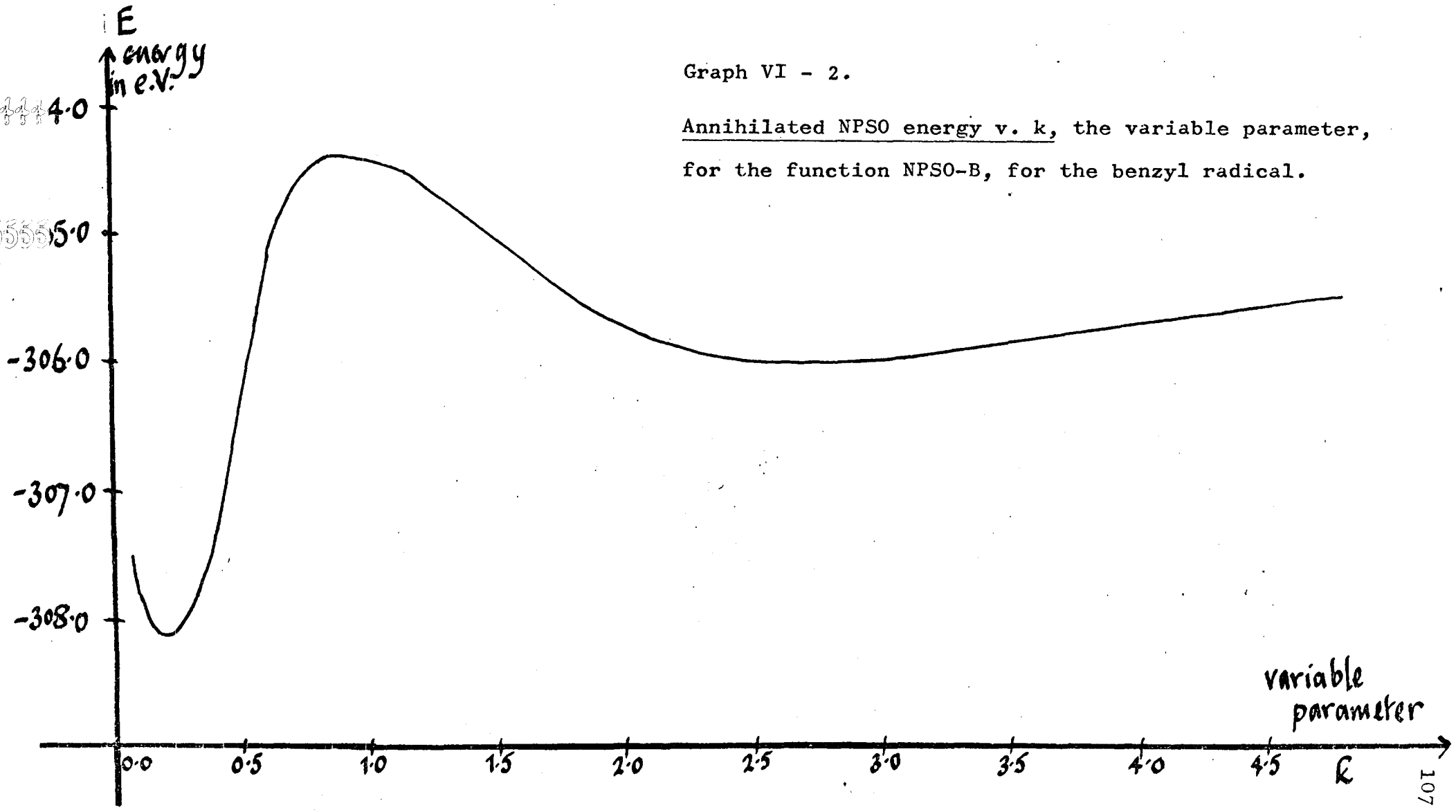
method	energy	k
MO (eigenvectors of the overlap matrix)	-303.9154 e.V.	
RHF - MO	-305.6740 e.V.	
UHF - MO	-308.8357 e.V.	
AMO	-308.6701 e.V.	λ = 0.5866
NPSO-A		
unprojected	-308.6047 e.V.	4.2
annihilated	-309.4675 e.V.	4.83
projected and annihilated	-309.5968 e.V.	4.85
projected and unprojected	-309.1104 e.V.	4.87
NPSO-B		
unprojected	-307.5750 e.V.	0.236
annihilated	-308.3498 e.V.	0.208
projected and annihilated	-308.4520 e.V.	0.209
projected and unprojected	-307.9956 e.V.	0.205

Table VI-5



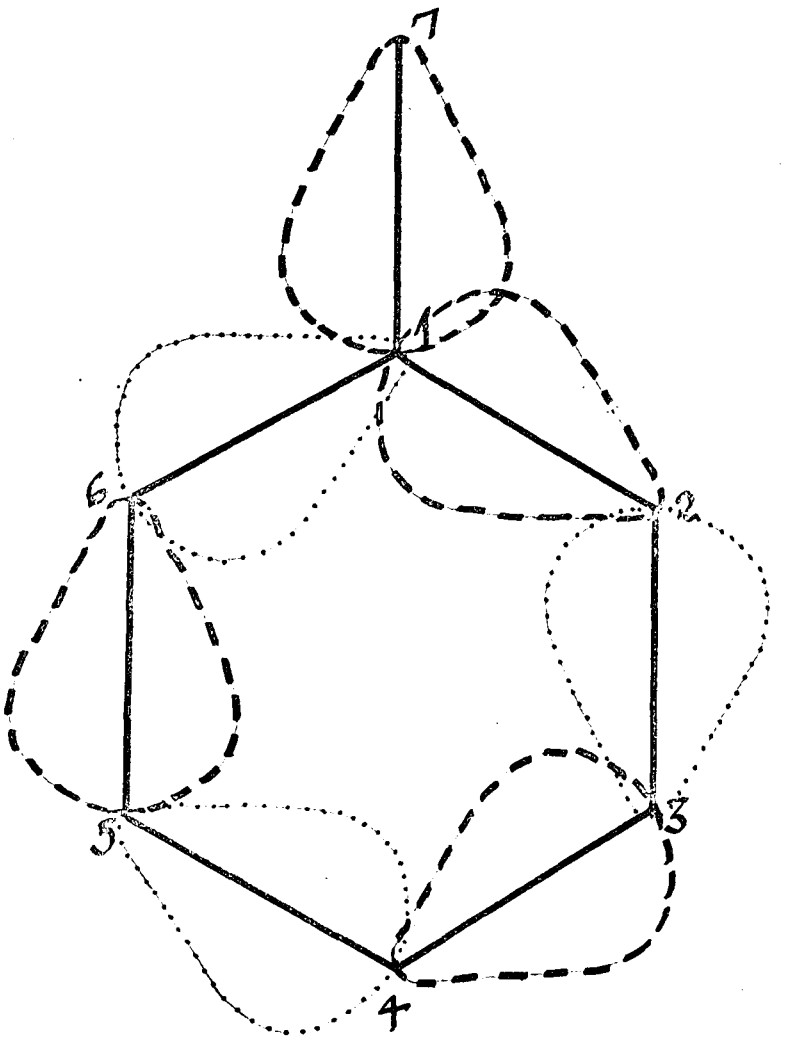
Graph VI - 1.

Annihilated NPSO energy v. k, the variable parameter, for the function NPSO-A, for the benzyl radical.



Graph VI - 2.

Annihilated NPSO energy v. k, the variable parameter, for the function NPSO-B, for the benzyl radical.

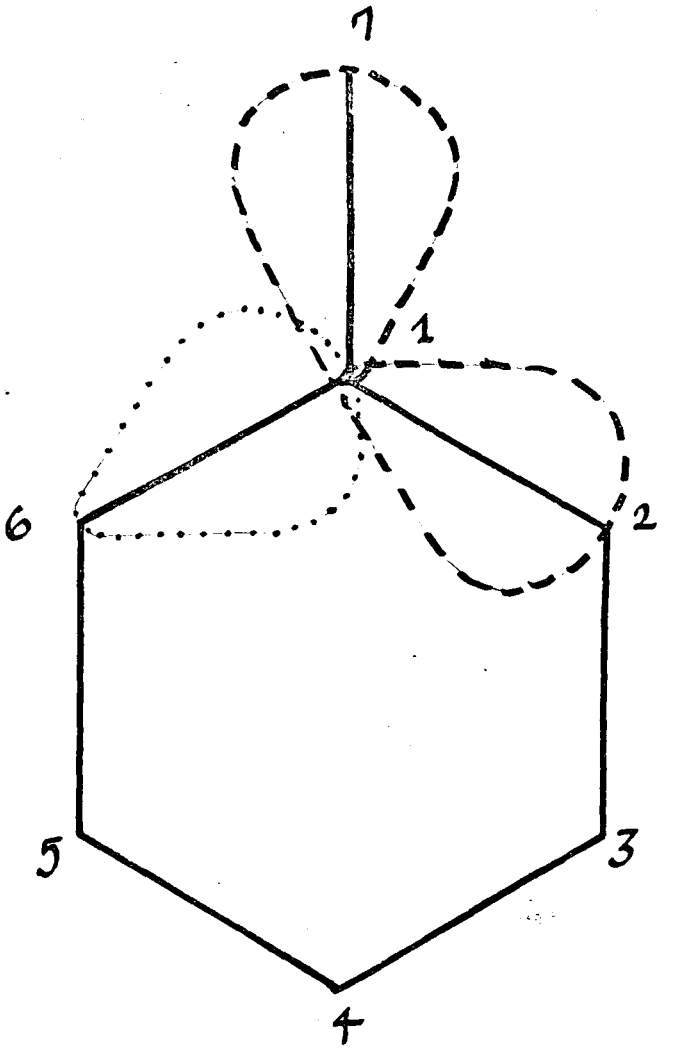


denotes a one-electron orbital containing an α electron

denotes a one-electron orbital containing an β electron

Figure VI-E

The representation of NPSO-A wavefunction, with $k < 1$.



denotes a one-electron orbital containing a α electron

denotes a one-electron orbital containing a β electron

Figure VI-F

The representation of NPSO-A wavefunction, with k 7 1.

bonds, will have large amplitudes in the same region of space. This will lead to more α electron repulsion, than the situation in figure VI-F. Here k is greater than 1.0. (Only the atoms 1,2,6 and 7 are considered, since for the ring atoms the bonds will be localised in different regions of space correctly.) The α repulsions in figure VI-F are minimised. Thus the energy given by this wavefunction, NPSO-A, if k is greater than 1.0 would be expected to be lower than that if k is less than 1.0 . Graph VI-1 shows this is so. The two minima are:-

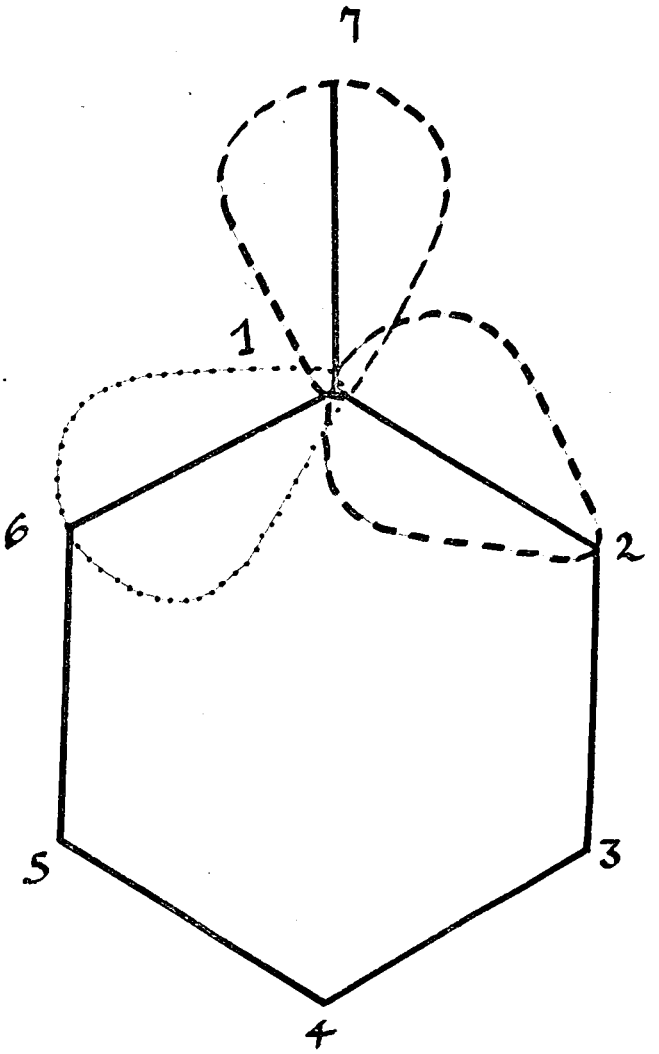
k	energy, in e.V.
0.214	-306.0977 e.V.
4.83	-309.4675 e.V.

ii) Wavefunction NPSO-B:

$$\psi_{1(B)} = A\,|(\chi_1 + k\chi_2)\alpha\,(\chi_3 + k\chi_4)\alpha\,(\chi_5 + k\chi_6)\alpha\,(\chi_7 + k\chi_1)\alpha\,(\chi_2 + k\chi_3)\beta\,(\chi_4 + k\chi_5)\beta\,(\chi_6 + k\chi_1)\beta\,| \qquad ..6\text{-}2$$

The minima for this wavefunction can be represented by figure VI-G, if k is less than 1.0, and figure VI-H, if k is greater than 1.0.

In both cases the α repulsions will not be minimised; but they will be lower than those of figure VI-E. If k is greater than 1.0, the $\alpha - \beta$ repulsions will be

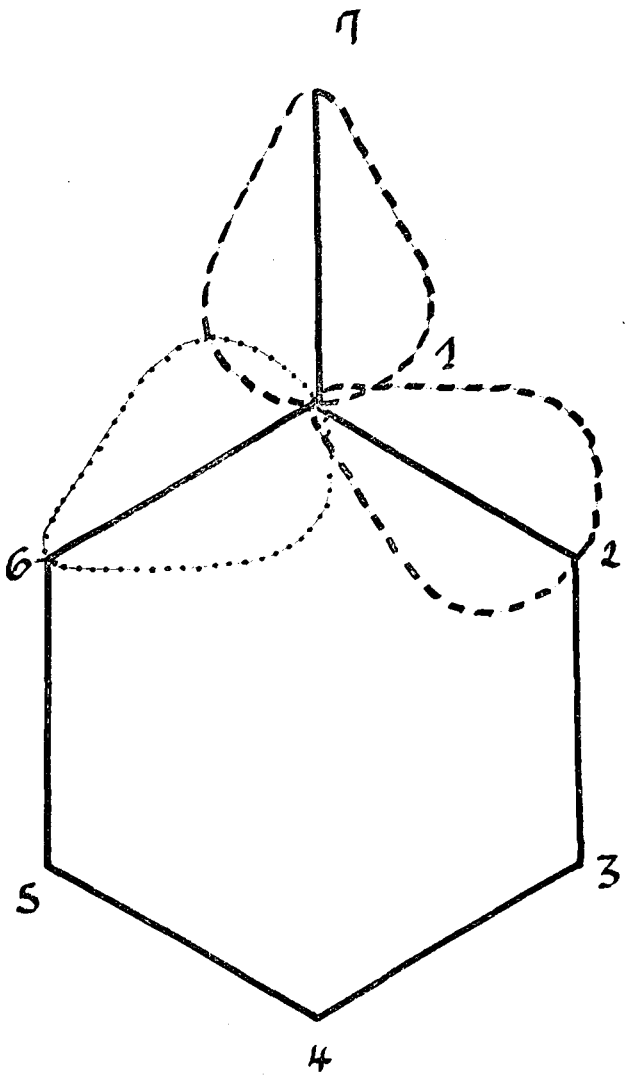


– – – – denotes a one-electron orbital containing a α electron

..... denotes a one-electron orbital containing a β electron

Figure VI-G

The representation of NPSO-B wavefunction, with $k < 1$.



▬▬▬ denotes a one-electron orbital containing a α electron

····· denotes a one-electron orbital containing a β electron

Figure VI-H

The representation of NPSO-B wavefunction, with $k > 1$.

greater than if k is less than 1.0 . Thus, of the two energy minima for this NPSO wavefunction, that for k greater than 1.0 should be higher than that for k less than 1.0 ; the actual values are:-

k	energy in e.V.
0.208	-308.3498 e.V.
2.65	-306.1861 e.V.

Thus empirically it is possible to predict the relative order of the energies of the various NPSO wavefunctions, in agreement with the order found. That is:-

NPSO-A ($k>1$), NPSO-B ($k<1$), NPSO-B ($k>1$), NPSO-A ($k<1$).

From table VI-5 it can be seen that the UHF-SCF-MO and AMO energies are better than that of the unprojected NPSO method. This is in contrast to to the earlier results. However the AMO method does include full spin projection, whereas no allowance for spin projection has been made in the NSPO wavefunction - even interchange of α and β spin were not included, as previously. Inclusion of some spin projection, or annihilation, improves the NPSO energy - such that the NPSO method now gives reasonable energy lowerings. From these results it is possible to substantiate further that equation 3-52

- the projected and unprojected NPSO method - is a reasonable approximation to full spin projection.

VI.5: Further UHF Calculations.

Although the UHF energy was reasonable, the SCF-MO's were not as expected. The orbitals containing electrons of α spin, ψ_i for $i=1,..4$, in table VI-3, have the expected symmetry, but the β orbitals, ψ_i for $i=5,..7$, do not. Also the coefficients of some β orbitals seem large. Because of this we were prompted to investigate further.

i) The UHF program was tested on other molecules. The results for naphthalene and azulene (previously quoted), showed energy lowerings from the MO energy. Also the SCF-MO's had the expected symmetry. The MO's obtained for naphthalene agreed with the SCF-MO's of Pauncz,(75).

ii) With the same integral approximations, we calculated the RHF-MO's for the ions $C_6H_5CH_2^+$ and $C_6H_5CH_2^-$. We then used these orbitals as starting orbitals for a UHF calculation for the benzyl radical. The α orbitals were set equal to the RHF orbitals for the $C_6H_5CH_2^-$ ion, while those for the β electrons were set equal to the $C_6H_5CH_2^+$ ion RHF-MO's.

The results of the UHF calculation differed very little from the original UHF results; both the

molecular orbitals and the energy were little affected - table VI-5.

iii) We performed the UHF calculations using a further integral approximation - PPP data,(94). The integrals used are given in table VI-6; the only multi-centred integrals included were the two-electron coulomb integrals.

As a reference energy, we used that calculated by the SCF-MO program of J.E.Bloor and B.K.Gilson,(95). This gave an RHF energy. Our RHF program gave results equivalent to those of Bloor and Gilson - see table VI-7. We calculated the UHF energy, which gave the expected lowering from the RHF energy. The SCF-MO's resulting from the UHF calculation had the expected, correct, symmetry, see table VI-8. We thus continued to use the PPP data for NPSO calculations.

The unprojected energy was calculated, and that NPSO energy suggested as a close approximation to full spin projection. These results are also given in table VI-7; they are very disappointing.

Various reasons can be suggested for the lack of success of the NPSO:-

i)neglecting the multicentre integrals greatly affects the relative results of the various methods;

ii) using semi-empirical data with the NPSO method is unsatisfactory.

Pariser, Parr and Pople integral values for the benzyl radical.

element	coulomb integral	overlap integral
11	11.13	1.0
12	9.0285	0.24682
13	5.6511	0.0
14	4.9499	0.0
34	9.0285	0.24682
37	3.7995	0.0
47	3.3676	0.0

Matrix elements of the Hamiltonian were calculated within the Bloor and Gilson program. The input data set $H_{pp} = 0.0$, and calculated $H_{pp} = -\sum_{j}(jj \mid pp)$. $H_{pq} = 0.0$.

Table VI-6

Energy results for the benzyl radical, (PPP data).

all values quoted in e.V.

method	energy	k
MO (eigenvectors of the overlap matrix)	-227.5048 e.V.	
SCF -MO [a] (Bloor and Gilson)	-149.5799 e.V.	
SCF - MO		
RHF	-227.6979 e.V.	
UHF	-227.7850 e.V.	
NPSO unprojected	-224.1008 e.V.	1.4
projected and unprojected	-225.0770 e.V.	1.41

[a] Bloor and Gilson data defined $H_{pp} = -\sum_j (jj \mid pp)$;
the data in this work defined $H_{pp} = W_p - \sum_j (jj \mid pp)$,
hence the energy difference.

Table VI-7

Molecular orbitals for the benzyl radical, (PPP data).

Bloor and Gilson results

atom nos.	1	2 ± 6	3 ± 5	4	7	symmetry (a or s)
molecular orbital.						
1	0.4257	0.3971	0.3990	0.3989	0.1590	s
2	-0.5640	-0.2236	0.3010	0.5610	-0.2910	s
3	0.0	-0.5	-0.5	0.0	0.0	a
4	0.0	-0.2900	0.0	0.2260	0.8830	s

RHF results, this work

atom nos.	1	2 ± 6	3 ± 5	4	7	symmetry (s or a)
molecular orbital.						
1	-0.4260	0.3970	-0.3990	-0.3989	-0.1590	s
2	0.5640	0.2237	-0.3010	-0.5620	0.2909	s
3	0.0	0.5	0.4999	0.0	0.0	a
4	0.0	0.2906	0.0	-0.2260	0.0	s

Table VI-8. ....continued.

Molecular orbitals for the benzyl radical. ...continued.

UHF results, this work.

atom nos.	1	2 ± 6	3 ± 5	4	7	symmetry (a or s)
molecular orbital.						
1	0.4647	0.4114	0.3509	0.3492	0.2782	s
2	0.4286	0.0650	-0.3155	-0.5390	0.5643	s
3	0.0	-0.5321	-0.4657	0.0	0.0	a
4	-0.1558	-0.3877	0.6934	0.4283	0.6943	s
5	-0.4744	-0.3877	-0.3931	-0.3648	-0.1799	s
6	0.5924	0.1613	-0.3435	-0.5208	0.2997	s
7	0.0	-0.4658	-0.5320	0.0	0.0	a

Table VI-8.

VI.6: Further Integral Approximations.

Amos and Burrows (96) also noticed that, during their calculations on the benzyl radical, the integrals used significantly affected the results. We thus continued our calculations using different integral approximations, including various two-electron integrals. Perhaps this could resolve the anomolous nature of the UHF orbitals.

i) Goeppert-Mayer and Sklar Data.

Here the one-electron core integrals were calculated by the method of Goeppert- Mayer and Sklar,(97). The one centre coulomb integrals were set equal to 17.230664e.V. Other two centre coulomb integrals were calculated by P.H.Martin. All other two electron integrals were neglected. Complete overlap was included. See appendix II. Values are given in table VI-9.

ii) After Karplus and Shavitt, (98).

The Ruedenberg approximations were used for calculating the overlap, one-electron and one centre coulomb integrals. However, to correspond with Karplus and Shavitt's calculations the internuclear distance was set equal to 1.39 Å, and the orbital exponent to 1.590. The two centred coulomb, hybrid and exchange integrals were provided by P.H.Martin. All other multicentre integrals, with the exception of the exchange and hybrid integrals between neighbours and next-nearest neighbours, were set equal to zero.

Integral values for the benzyl radical,

Goeppert - Mayer Sklar data.

element	coulomb integral	overlap integral	matrix element of the Hamiltonian.
11	17.22703	1.0	-56.53317
22			-52.51440
33			-50.65466
44			-50.22048
77			-43.19203
12	9.02847	0.24682	-15.28695
13	5.65114	0.03470	-2.01159
14	4.94987	0.01545	-0.89232
37	3.79954	0.00193	-0.10046
47	3.36759	0.00059	-0.03026
17			-14.21777
23			-14.64157
24			-1.94545
25			-0.86956
26			-1.98509
27			-1.83476
34			-14.35969
35			-1.92084
36			-0.86956

Table VI-9

Karplus and Shavitt data, two centre integrals.

(accurate values)

element ij	coulomb integral (ii | jj)	exchange integral (ij | ij)	hybrid integral (ii | ij)
12	9.02731	0.92741	3.31222
13	5.66891	0.01722	0.37789
14	4.96759	0.00337	0.15767
37	3.81615	0.00005	0.01975
47	3.38243	0.000005	0.00575

Karplus and Shavitt data, three centre integrals.

(values from reference 98.)

elements ijk	exchange integral (ij | ik)	hybrid integral (ii | jk)
123	0.11186	1.85512
126	0.65091	0.43883

Table VI-10.

Integral values for the benzyl radical;

for Karplus and Shavitt data, and accurate three centre integrals.

element	matrix element of the Hamiltonian	overlap integral
11	-56.78766	1.0
22	-52.72065	
33	-50.85740	
44	-50.42367	
77	-43.34006	
12	-16.05165	0.25997
23	-15.37427	
34	-15.07706	
71	-14.92736	
31	-2.24359	0.03888
41	-1.01918	0.01773
42	-2.16988	
52	-0.99326	
53	-2.14230	
62	-2.21432	
72	-2.04620	
73	-0.12182	0.00236
74	-0.03789	0.00074

Table VI-11

Integral values for the benzyl radical;

Accurate three centre integrals.

atom nos.	exchange integral	hybrid integral
ijk	(ii jk)	(ij ik)
123	1.85514	0.11186
124	0.27207	0.04176
125	0.14734	0.08635
125	0.43883	0.65091
134	1.40548	0.00686
135	0.24063	0.01308
137	0.02406	0.07300
147	0.00732	0.03025
247	0.00593	0.00968
257	0.01540	0.00473
347	0.00529	0.00397
357	0.01363	0.00062
367	0.19614	0.00034
427	0.16921	0.00023
417	1.04813	0.00012
437	0.01286	0.00134
713	0.20803	0.00545
714	0.08932	0.00159
723	1.23680	0.00088
725	0.07779	0.00070
734	0.83411	0.000015
735	0.11590	0.000042

Table VI-12.

For these exchange and hybrid integrals we used the values given by Karplus and Shavitt. All values used are given in table VI-10. and table VI-11.

iii) Accurate three centre hybrid and exchange integrals.

Accurate three centre hybrid and exchange integrals, provided by D.M.Hirst, were used in conjunction with the two centre integrals provided by P.H.Martin. The four centre integrals were neglected. The coulomb one-electron and overlap integrals were calculated as in ii) above. The integrals are given in tables VI-11 and 12.

iv) Goeppert-Mayer and Sklar core and Mulliken approximation.

Here, as in i) the Goeppert-Mayer and Sklar approximation was used for the one electron integrals and the two centre integrals. The Mulliken approximation was used for all other two electron integrals.

Results and Discussion.

The results of the calculations - MO energy, UHF, RHF, AMO and various NPSO calculations - are given in table VI-13. From these it can be seen that the effectiveness of the NPSO method, and in some cases the AMO method, depends on the integrals used.

Using Goeppert-Mayer Sklar data with the Mulliken approximation, as with Ruedenberg's data and the Mulliken approximation, means that the NPSO energy,

Energy calculations for the Benzyl radical.

all values are given in e.V.

method of calculation of energy.	Ruedenberg integrals with Mulliken approximation.	Goeppert-Mayer Sklar integrals with Mulliken approximation.
MO	-303.9154	-218.8816
RHF	-305.6740	-219.8315
UHF	-308.8357	-223.1363
AMO	-308.6701	-223.5855
NPSO-A unprojected	-308.6047	-223.0043
annihliated	-309.4675	-223.8714
projected and unprojected	-309.1104	-223.5265
projected and annihliated	-309.5968	-223.9927
NPSO-B unprojected	-307.5750	-222.2996
annihilated	-308.3498	-223.0785
projected and unprojected	-307.4956	-222.7274
projected and annihilated	-308.4520	-223.1799

Table VI-13 ...continued.

Energy calculations for the Benzyl radical.

all values are given in e.V.

method of calculation of energy.	after Karplus and Shavitt.	including accurate three-centre integrals.
MO	-241.6057	-225.7354
RHF	-241.7148	-226.3019
UHF	-242.0171	-227.0121
AMO	-242.4686	-227.7843
NPSO-A		
unprojected	-236.9584	-225.9728
annihilated	-238.9605	-227.2753
projected and unprojected	-238.3351	-226.8292
projected and annihilated	-239.4480	-227.5716
NPSO-B		
unprojected	-235.8145	-224.9004
projected and unprojected	-237.3333	-226.0846

Table VI-13 ...continued.

Energy calculations for the Benzyl radical.
all values are given in e.V.

method of calculation of energy.	Ruedenberg core with GMS two centre integrals.	Goeppert-Mayer Sklar data.
MO	-345.3647	-258.1880
RHF	-346.5510	-261.0764
UHF	-346.6211	-261.1411
AMO	-345.7303	-260.7890 [1]
NPSO-A		
unprojected	-340.0596	-254.4292
projected and unprojected	-342.6255	-256.5845

Table VI-13

[1] obtained from eigenvectors of the overlap matrix as starting orbitals; using SCF-MO's gives -261.2599 e.V.

including some spin projection, is lower than the AMO energy; though the AMO method is better than the unprojected NPSO wavefunction. However, with Goeppert-Mayer Sklar data the partially spin projected NPSO, (projected and unprojected NPSO), fails to lower the energy below that of the AMO method, contrary to previous results.

The NPSO-B wavefunction is still not as good a wavefunction as NPSO-A. From these results it is possible to suggest that, if all multi-centred integrals are included, the NPSO wavefunction, when partially spin projected, gives good account of spin correlation.

From table VI-13, it can be seen that neglecting some of the multicentre two electron integrals reduces the effectiveness of the NPSO method, while that of the AMO is little reduced.

If all but nearest neighbour exchange and hybrid three centre integrals are neglected, as in approximation ii), the NPSO method fails to reduce the energy below that of the MO energy - whereas the AMO method is still more effective than the UHF method.

Using more accurate values for the three centre integrals - or including all of them - means that the NPSO without any spin projection now lowers the energy below that of the MO method. Including some spin projection means that the NPSO energy is lower than the UHF energy, and comparable to the AMO results.

Again it can be seen that NSPO-A wavefunctions are better than those of NPSO-B. Thus we performed no more calculations using NPSO-B wavefunctions.

The Goeppert-Mayer Sklar results - as with the PPP data, where all three and four centre integrals and some two centre integrals were neglected - are very poor. The AMO method lowers the energy from the MO energy, but even the RHF method gives a lower energy than it. The NPSO method, including some spin projection, is still not lower than the MO energy.

It has previously been noted that the Goeppert-Mayer Sklar and Mulliken data was not as successful as the Ruedenberg and Mulliken, To try to ascertain whether this poor performance using Goeppert-Mayer Sklar data is a function of the core integrals, or neglect of the multicentre integrals, we performed further calculations using data synthesised from previous values. The Ruedenberg core integrals were used (table VI-1) with the Goeppert-Mayer Sklar two centre hybrid and exchange integrals. All other two electron integrals were neglected. These results are also in table VI-13. They are comparable to those using complete Goeppert-Mayer Sklar data; suggesting that the reason for the poor performance of both the AMO and NPSO methods with Goeppert-Mayer Sklar data is the neglect of the multicentre two electron integrals. In this respect, the NPSO method seems more dependant on the integrals used than the AMO method.

These results suggest that good agreement between theory and experimental results will need the inclusion of many centre integrals. Indeed, neglect of three centre integrals has been previously criticised,(93).

Despite all the different sets of integrals we investigated, we were unable to explain the anomalous behaviour of the UHF orbitals previously discussed, though this was the prime reason for studying the different integral sets.

VI.7:Spin Densities.

i)Introduction:

Recently there has been considerable interest in the calculation of spin densities for conjugated hydrocarbon radicals. See for example,(42),(89). Despite the fact that to explain the hyperfine structure of an e.s.r. spectrum sigma - pi interactions must be considered, McConnell (99) deduced a relationship between the experimentally measured hyperfine coupling constant and the pi-electron spin density.

$$a_H = -Q \rho_\pi \qquad \text{..6-18}$$

where

a_H = hyperfine coupling constant

ρ_π = π - electron spin density

and Q is a constant of value $\simeq$ 20 - 30 gauss,(99).

Physically the spin density, ρ, is the difference between the probability of finding an electron of α spin over that of finding one with β spin in volume δv. Thus the spin density for a system described by an RHF wavefunction is given, simply, by the square of the coefficient of the singly occupied orbital.

One reason for the benzyl radical attracting so much attention is that, generally, the computed para proton splitting is less than that for the ortho - contrary to experimental results. Two exceptions have been found: the valence bond method, (100), and the UHF calculation of Berthier and Baudet, (101). However the valence bond method gives poor overall agreement with experiment; and another UHF calculation, that of Amos and Snyder, (42), predicts the ortho - para ratio incorrectly. Carrington and Smith, (87), suggest that the discrepancy between the two UHF methods was a function of the data used.

ii) Calculations:

We calculated the spin densities by various methods.

a)RHF method.

Here, as with the HMO method, (102), since the spin densities are given by the squares of the coefficients of the singly occupied orbitals, it is not possible to obtain negative spin densities.

b) UHF method.

Here the spin densities, s, are calculated from

$$S_r = \sum_{i=\alpha} C_{ri}^2 - \sum_{j=\beta} C_{rj}^2 \qquad ..6\text{-}19$$

Negative spin densities can thus be obtained. Amos and Snyder, (42), have performed similar UHF calculations - but with different integral approximations, and have included annihilation of contaminating spin functions in the UHF wavefunction. Some of their results are quoted in table VI-14.

Because of the unusual form of our UHF orbitals the spin densities we obtained were unreasonable. However, if the MO's are annihilated to remove the triplet spin function the spin densities thus obtained were quite reasonable.

c) We performed AMO calculations by two similar methods. We used Paunz's formula for a normalised fully spin projected single determinant of the form of equation 6-17.

$$\langle\psi|\rho|\psi\rangle = \frac{1}{2}\left[\frac{S}{S+1}\left\{\sum_{i=1}^{\nu}\left(\sum_{r=0}^{\nu-i}(-1)^r C_r {}^1S_r\left(a_I^2(0) - a_{\bar{I}}^2(0)\right)\right)\right.\right.$$
$$-\sum_{r=0}^{\nu-1}(-1)^{r+1} C_{r+1} {}^1S_r\left[2\,a_I^2(0) + a_I^*(0)\,a_{\bar{I}}(0)\,\lambda_i + a_{\bar{I}}^*(0)\,a_I(0\right.$$
$$\left.\left.+\sum_{i=\nu+1}^{\mu}\left(\psi_i^2(0)\sum_{r=0}^{\nu}(-1)^r\left(C_r - 2C_{r+1}\right)S_r\right\}\right]$$

..6-20

where C_r, S_r and ${}^1S_r$ are defined as previously.
ν and μ denote number of β and α electrons, respectively.

Results of the spin density calculations for the benzyl radical.

Ruedenberg Data:

method	1	2	3	4	7
RHF	0.006	0.065	0.000	0.030	0.850
UHF	-0.782	0.853	-0.841	0.842	0.789
annihilated					
UHF	-0.264	0.429	-0.268	0.423	0.401
AMO	-0.264	0.451	-0.270	0.455	0.537
projected and annihilated					
NPSO-A	-0.589	0.696	-0.594	0.687	0.709
NPSO-B	0.356	-0.296	0.339	-0.293	0.410
projected and unprojected					
NPSO-A	-0.483	0.616	-0.501	0.604	0.658

Goeppert Mayer Sklar Data:

RHF	0.002	0.031	0.000	0.014	0.960
AMO	-0.263	0.450	-0.269	0.454	0.538
projected and annihilated					
NPSO-A	-0.619	0.718	-0.618	0.711	0.722
projected and unprojected					
NPSO-B	-0.516	0.641	-0.530	0.631	0.673
Experimental hyperfine coupling constant (gauss)		5.14	1.75	6.14	16.35

Table VI-14.

The formula given in reference 67, (equation 6-72) contains typographical errors.

The Harris formula,(103), also for a normalised wavefunction is

$$\langle\psi|\rho|\psi\rangle = (N!)^{-1}\left(\frac{2s+1}{n_\alpha+1}\right)\left(\frac{n_\alpha S}{2s+2}\right)\sum_{J=1}^{n_\alpha}\sum_{k}\binom{n_\alpha}{k}^{-1}\Delta_k^J$$
$$\left[\left(\frac{n_\alpha+k+2}{n_\alpha-k}\right)\left|\chi_J^2(0)-\bar{\chi}_J^2(0)\right|\right.$$
$$\left.-\left(\frac{k+1}{n_\alpha-k}\right)\Delta_J\left(\vec{\chi}_J(0)\,\chi_J(0)+\chi_J^*(0)\,\bar{\chi}_J(0)\right)\right] \quad \text{..6-21}$$

Here the normalisation differs from that of Pauncz. $\bar{\chi}_J$ is set equal to zero if J is greater than the number of β electrons. However it should be noted that the recursion formulae given for Δ_k and Δ_k^J are incorrect; Δ_k and Δ_k^J are defined as in equation 6-10.

d) Both NSPO wavefunctions $\psi_{(A)}$ and $\psi_{(B)}$, equations 6-1 and 6-2, were used to calculate the spin densities, to the two approximations of full spin projection - unprojected and projected, and projected and annihilated NPSO. In both cases we used the Pauncz,(and Harris) formula for the spin projection of the single determinant;and calculated the cross terms, $\langle\psi_1|\rho|\psi_1\rangle$ and $\langle\psi_1|\rho|A_s\psi_1\rangle$ separately, taking the sum of the α spin densities minus the sum of the β spin densities, and in the case of annihilation, summing over all twelve possible determinants.

All calculations were performed using both the Ruedenberg core integrals and the Goeppert-Mayer Sklar core approximations; Mulliken's approximation was

used for the multicentre two electron integrals, and full overlap was included.

iii)Results:

The spin density results are given in table VI-14. The wavefunction NSPO-B gives spin densities of the wrong sign, and since the energy of this wavefunction is not the minimum, these results can be discarded.

The UHF spin densities are too large - but since the UHF-MO's were incorrect, it seems not unreasonable to reject these, too.

Neither the AMO results or the NPSO ones are in very good agreement with experimental results, though those of the AMO method seem better than the NPSO results. The NPSO method over-estimates the spin density on the ring atoms.

iv) Two parameter NPSO wavefunctions:

In an effort to improve the NPSO spin density results - increase that of the 7 th. atom and reduce the spin density on the ring atoms - a two parameter NPSO wavefunction was written, one parameter, k, for the ring atoms and another, k_t, for the 7 th. atom.

The initial wavefunction was

$$\psi_1(A) = A\big|(\chi_1+k\chi_2)(1)\alpha(1)\ (\chi_3+k\chi_4)(2)\alpha(2)\ (\chi_5+k\chi_6)(3)\alpha(3)\ (\chi_7+k_t\chi_1)(4)\alpha(4)\ (\chi_2+k\chi_3)(5)\beta(5)\ (\chi_4+k\chi_5)(6)\beta(6)\ (\chi_6+k\chi_1)(7)\beta(7)\big| \quad ..6\text{-}22$$

Again a symmetry projection and a spin projection operator must be applied to equation 6-22 to give the total NPSO wavefunction as

$$\psi_T(A) = O_D(\psi_I(A) + \psi_{II}(A)) \qquad ..6\text{-}23$$

where

$$\psi_{II}(A) = A\,|(\chi_4+k\chi_{11})(1)\alpha(1)\ (\chi_5+k\chi_4)(2)\alpha(2)\ (\chi_3+k\chi_2)(3)\alpha(3)\ (\chi_1+k_t\chi_7)(4)\alpha(4)\ (\chi_2+k\chi_1)(5)\beta(5)\ (\chi_4+k\chi_3)(6)\beta(6)\ (\chi_6+k\chi_5)(7)\beta(7)\,| \qquad ..6\text{-}24$$

We also set up another NPSO wavefunction of the type NPSO-B, as previously discussed:

$$\psi_I(B) = A\,|(\chi_1+k\chi_2)(1)\alpha(1)\ (\chi_3+k\chi_4)(2)\alpha(2)\ (\chi_5+k\chi_6)(3)\alpha(3)\ (\chi_7+k_t\chi_1)(4)\alpha(4)\ (\chi_2+k\chi_3)(5)\beta(5)\ (\chi_4+k\chi_5)(6)\beta(6)\ (\chi_6+k\chi_1)(7)\beta(7)\,| \qquad ..6\text{-}25$$

and from this the total NPSO-B wavefunction was given by

$$\psi_T(B) = O_D(\psi_I(B) + \psi_{II}(B)) \qquad ..6\text{-}26$$

where

$$\psi_{II}(B) = A\,|(\chi_1+k\chi_6)(1)\alpha(1)\ (\chi_5+k\chi_4)(2)\alpha(2)\ (\chi_3+k\chi_2)(3)\alpha(2)\ (\chi_7+k_t\chi_1)(4)\alpha(4)\ (\chi_2+k\chi_1)(5)\beta(5)\ (\chi_4+k\chi_3)(6)\beta(6)\ (\chi_6+k\chi_5)(7)\beta(7)\,| \qquad ..6\text{-}27$$

Energy calculations for the Benzyl radical - using NPSO wavefunctions with two variable parameters.

all values are given in e.V., for energy.

Using Ruedenberg core with the Mulliken approximation:

	energy	k	k_t
NPSO-A	-309.1934	5.4	2.95
NPSO-B	-308.0751	0.8	0.8

Using Goeppert-Mayer Sklar core with Mulliken approximation:

	energy	k	k_t
NPSO-A	-223.5427	5.45	7.7

Table VI-15.

Results of the spin density calculations for the benzyl radical, using NPSO wavefunctions with two variable parameters.

Using Ruedenberg core with the Mulliken approximation:

	1	2	3	4	7
NPSO-A	-0.483	0.616	-0.501	0.604	0.658

Using Goeppert-Mayer Sklar core with the Mulliken approximatio

NPSO-A	-0.413	0.630	-0.521	0.621	0.693

Table VI-16.

Ruedenberg integrals,with Mulliken's approximation, were used to calculate the minimum energy for both functions. The suggested approximation to full spin projection was used - projected and unprojected NPSO. The results are given in table VI-15. Again it can be seen that the NPSO-A wavefunction gives a lower energy than that of type B . The Goeppert-Mayer Sklar data and the Mulliken approximation was used to calculate the energy minimum for wavefunction NPSO-A. These results are also given in table VI-14.The spin density results for both integral approximations are given in table VI-16. As previously the results using an NPSO wavefunction type B must be rejected.

There is very little improvement in the spin density results, and the small reduction in the energy, less than 0.1 e.V., is possibly not worth the effort needed to introduce a second variable parameter into the NPSO wavefunction.

v)Discussion:

Several reasons for the poor agreement between the spin density calculations and experimental results can be suggested.

a) The validity of the McConnell relationship (99) has been questioned, since Q , the constant relating the experimentally measured hyperfine coupling constant with the calculated spin density, is usually given an average value. Carrington and Smith (87) pointed out that, if a different value of Q is used for the ring atoms, to that for the CH chain atom, the agreement between theoretical and

experimental spin densities improves. Several attempts have now been made to try to redefine the McConnell relationship,(104),(105); but none has, as yet, replaced it.

b) The assumed geometry has recently been questioned,(91). Benson and Hudson (106) noted that relaxing the assumed geometry led to a marked improvement in the theoretical coupling constants; while Beveridge and Guth (107) calculated the theoretical geometry - this deviated considerably from the assumed geometry. However it is thought that altering the geometry of the radical would not much affect the NPSO results.

c) It has been noted (108) that for the allyl radical, methods which use localised orbitals in spin density calculations tend to give results which are too high. Perhaps use of localised - or as in the case of the NPSO method semi-localised - orbitals adversely affects the spin density calculations.

d) The omission of full spin projection for the NPSO method may be a gross over-simplification, for spin density calculations. We have already noted that annihilation has been criticised,(39).

e) The integrals used have, also, previously been questioned; perhaps these also adversely affect the results. Amos and Snyder (42) noted that annihilation is a satisfactory approximation for calculations with Pariser, Parr and Pople data, but that using theoretical integral values gives

spin properties in poor agreement with experiment. Also Hansen (109) suggested that electron correlation effects explicitly included in ab initio methods are often implicitly included in semi-empirical methods. With this in mind some later calculations used further semi-empirical data.

VII. FURTHER APPLICATIONS OF THE NPSO METHOD.

VII.1: Introduction.

Preliminary calculations were performed to extend the NPSO method to various open shell systems, butadiene ions, both cis and trans, the pentadienyl radical, azulene negative ion and naphthalene negative ion, with a view to calculating the spin densities. These spin densities are then be compared to those of Amos and Snyder, (42). Amos and Snyder's results have been previously compared to other methods, (11).

Throughout these calculations the integrals used were those calculated by Ruedenberg's method, appendix I, with the Mulliken approximation for multi-centred integrals.

The MO energy was calculated, using equation 6-14 with eigenvectors of the complete overlap matrix as orbitals. This result was then compared to that for the NPSO method. We chose to calculate the NPSO energy within the unprojected approximation - thus no allowance was made for spin projection.

If the symmetry projected NPSO wavefunction is ψ_T,

$$\psi_T = O_S [\psi_I + \psi_{II}] \qquad ..7\text{-}1$$

in general the unprojected NPSO wavefunction will give the total energy as

$$E = \frac{\langle \psi_I | H | \psi_I \rangle + \langle \psi_I | H | \psi_{II} \rangle}{\langle \psi_I | \psi_I \rangle + \langle \psi_I | \psi_{II} \rangle} \qquad ..7\text{-}2$$

For previous calculations this approximation has been shown to give a reasonable energy lowering from the MO energy; it should thus give a fair indication of the energy lowering the NPSO method would give for any system.

VII.2: Pentadienyl Radical.

The geometry of the radical was assumed regular - bond length of 1.4 Å, bond angle of 120°. The numbering used was that of Amos and Snyder; see figure VII-A.

The initial NPSO wavefunction was written as

$$\psi_I = A\left| \chi_1(1)\alpha(1)\ (\chi_2 + k\chi_3)(2)\alpha(2)\ (\chi_4 + k\chi_5)(3)\alpha(3)\ (\chi_1 + k\chi_2)(4)\beta(4)\ (\chi_3 + k\chi_4)(5)\beta(5) \right| \quad ..7\text{-}3$$

The application of the symmetry projection operator for the C_2 point group gives ψ_T as the ground state wavefunction.

$$\psi_T = [\psi_I + \psi_{II}] \quad ..7\text{-}4$$

where

$$\psi_{II} = A\left| \chi_5(1)\alpha(1)\ (\chi_4 + k\chi_3)(2)\alpha(2)\ (\chi_2 + k\chi_1)(3)\alpha(3)\ (\chi_5 + k\chi_4)(4)\beta(4)\ (\chi_3 + k\chi_2)(5)\beta(5) \right| \quad ..7\text{-}5$$

Here substituting $1/k$ for k in the wavefunction will not leave the wavefunction unchanged.

The integrals used in the calculation are given in table VII-1a; the results in table VII-1b.

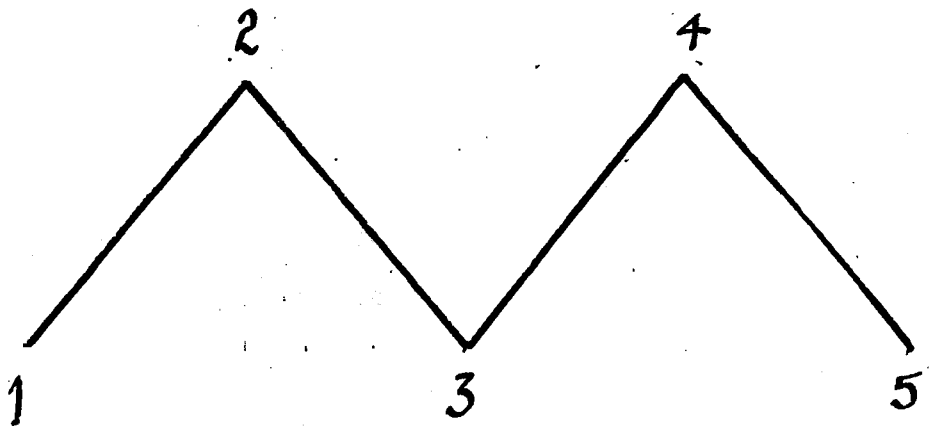


Figure VII-A

the numbering scheme for the pentadienyl radical.

Integral Values for the Pentadienyl Radical

element	coulomb integral	overlap integral	matrix element of Hamiltonian
11	17.22702	1.0	-44.84189
22	17.22702	1.0	-52.78417
33	17.22702	1.0	-54.63513
12	9.02847	0.24682	-14.00477
13	5.65114	0.03470	-1.47877
14	3.80018	0.00194	-0.08074
15	2.92895	0.00012	-0.00452
23			-14.98594
24			-1.55249

all values not given above can be generated by consideration of the symmetry of the radical

Table VII-1a

The energy and spin density results for the Pentadienyl radical.

Energy results:

MO energy	-183.2767 e.V.	
NPSO energy	-187.0666 e.V.	k = 4.785

Table VII-1b.

Spin density results:

method of calculation:	atom number: 1 & 5	2 & 4	3
Amos and Snyder[1]	0.545	-0.307	0.524
NPSO	0,465	-0.427	0.430

Table VII-1c.

[1] reference 42.

As expected the unprojected NPSO wavefunction gives a lower energy than the MO wavefunction.

The spin density results , in table VII-1c, show some resemblance to those of Amos and Snyder,(42), for a single determinantal wavefunction. The third atom has a greater spin density than that of the first atom. But , as Amos and Snyder noted, the unannihilated spin density appears to give too large a separation of the positive and negative spin densities; our method shows ths same trait. Perhaps use of the annihilated NPSO would improve the spin density results; it should also give a slightly larger energy lowering.

VII.3:The Butadiene Ions.

A:Trans Butadiene Negative Ion.

The geometry was assumed regular, and along with the numbering scheme is shown in figure VII-B.

The initial NPSO wavefunction was set up as

$$\psi_I = A\left| \chi_1(1)\alpha(1)\ (\chi_2+k\chi_3)(2)\alpha(2)\ \chi_4(3)\alpha(3)\ (\chi_1+k\chi_2)(4)\beta(4)\ \ (\chi_3+k\chi_4)(5)\beta(5)\right| \quad ..7\text{-}6$$

From the point group of the ion - C_{2h} - the total NPSO wavefunction, without spin projection, is

$$\psi_T = \psi_I + \psi_{II} \quad ..7\text{-}7$$

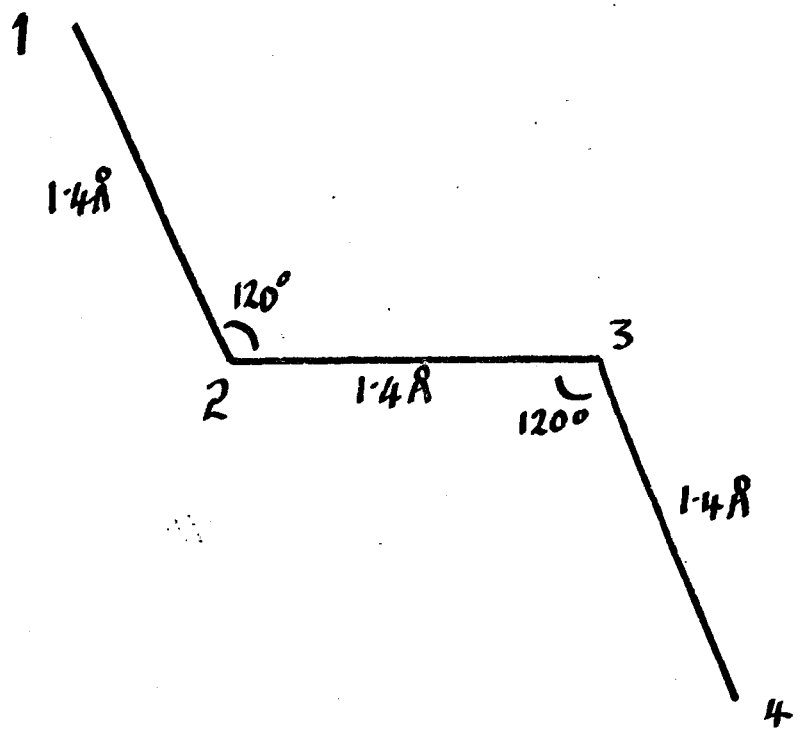


Figure VII-B

the numbering scheme for the trans-butadiene negative ion.

Integral values for the trans butadiene negative ion.

element	coulomb integral	overlap integral	matrix element of the Hamiltonian.
11	17.22703	1.0	-40.07019
22	17.22703	1.0	-47.14124
12	9.02847	0.24682	-13.17432
13	5.65114	0.03470	-1.32989
14	3.80018	0.00193	-0.06916
23			-13.81955

all integral values not quoted here can be generated by considering the symmetry of the ion.

Table VII-2a

The results of the energy calculation for the trans butadiene negative ion.

method of calculation		
MO	-139.85521	
NPSO 'B'	-139.00066	k = 2.61
NPSO 'A'	-140.26711	k = 2.545
NPSO (symmetric)	-140.26711	k = 2.55

Table VII-2b

The results of the spin density calculations for the trans butadiene ion.

method of calculation	atom number 1 & 4	2 & 3
Amos and Snyder[1]	0.457	0.043
NPSO 'B'	0.561	0.026
NPSO 'A'	0.918	-0.264
NPSO (symmetrical)	0.915	-0.346

[1] reference 42.

Table VII-2c.

where

$$\psi_{II} = A\left|\begin{array}{cc} \chi_4(1)\alpha(1) & (\chi_3 + k\chi_2)(2)\alpha(2) \quad \chi_1(3)\alpha(3) \\ (\chi_4 + k\chi_3)(4)\beta(4) & (\chi_2 + k\chi_1)(5)\beta(5) \end{array}\right| \quad ..7\text{-}8$$

The integrals used are given in table VII-2a, and the results in table VII-2b.

Here the wavefunction is unaltered by substituting $1/k$ for k.

The results show that the NPSO wavefunction does not lower the energy from that of the MO wavefunction. From empirical considerations, perhaps, this can be explained. A diagramatic representation of the NPSO wavefunction may be given as in figure VII-C.

From this it can be seen that the $\alpha - \beta$ spin repulsions could be described as : two small repulsions, on and around atoms 2 and 3; one slightly larger repulsion, on and around atom 1, and one large $\alpha - \beta$ repulsion, on atom 4.

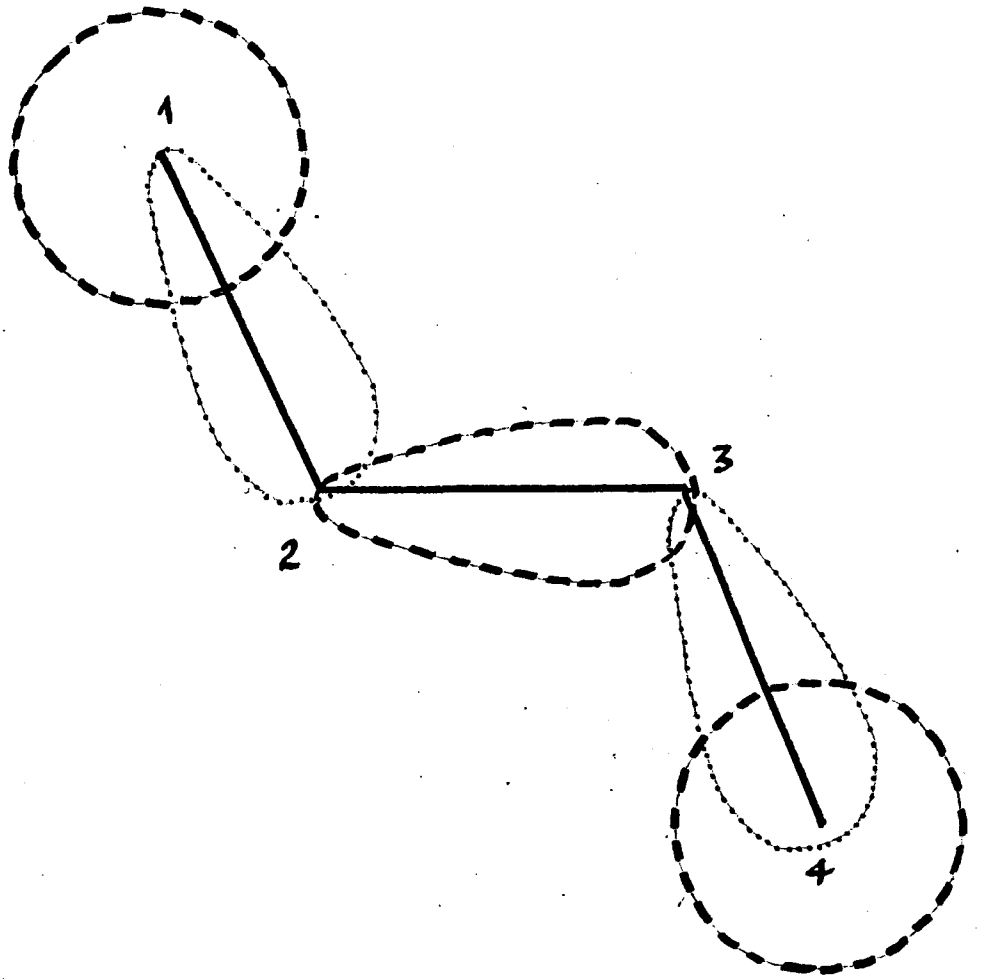
There are two possible ways of re-writing the wavefunction, NPSO-A, see figure VII-D,and symmetrical NPSO, see figure VII-E. These give the following unprojected wavefunctions:

in each case,

$$\psi_T = \psi_I + \psi_{II} \quad ..7\text{-}7$$

for variant NPSO-A

$$\psi_I = \left|\begin{array}{cc} \chi_1(1)\alpha(1) & (\chi_2 + k\chi_3)(2)\alpha(2) \quad \chi_4(3)\alpha(3) \\ (\chi_1 + k\chi_2)(4)\beta(4) & (\chi_4 + k\chi_3)(5)\beta(5) \end{array}\right| \quad ..7\text{-}9$$

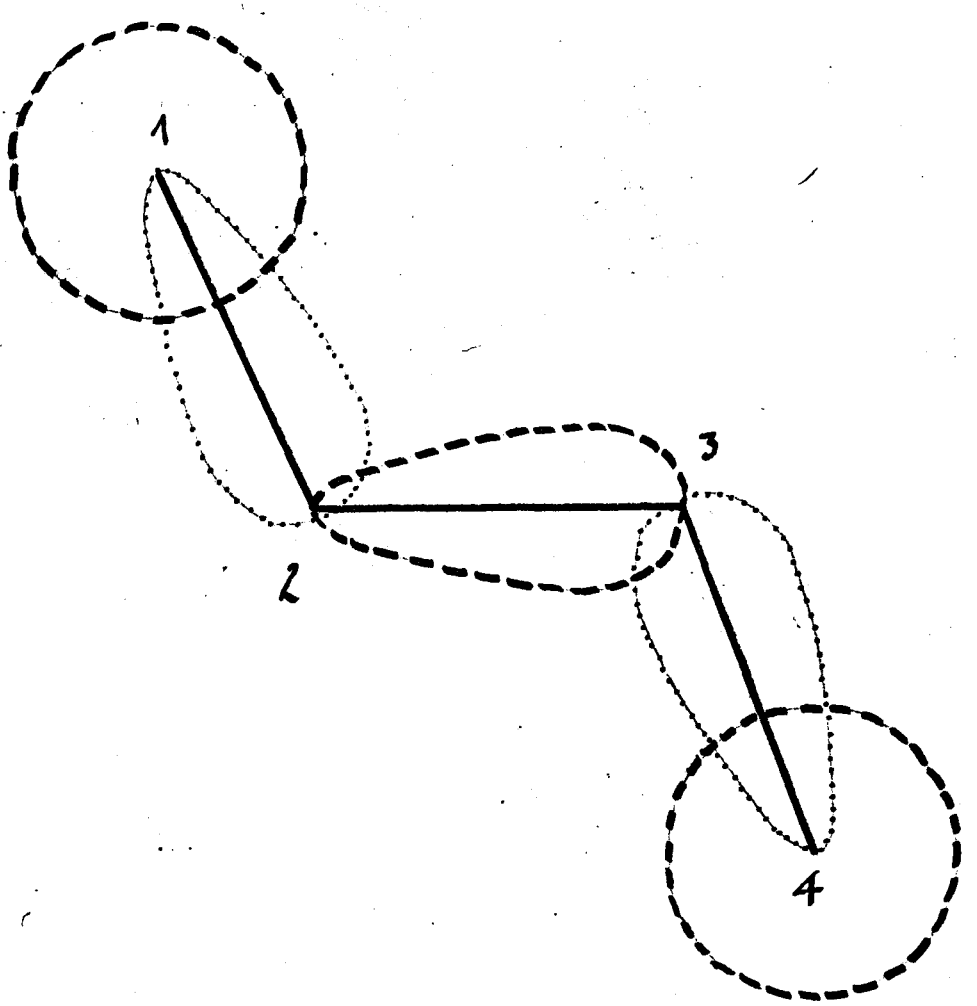


denotes a one-electron bond containing a α electron

denotes a one-electron bond containing a β electron.

Figure VII-C

The representation of the NPSO wavefunction for the trans butadiene ion.

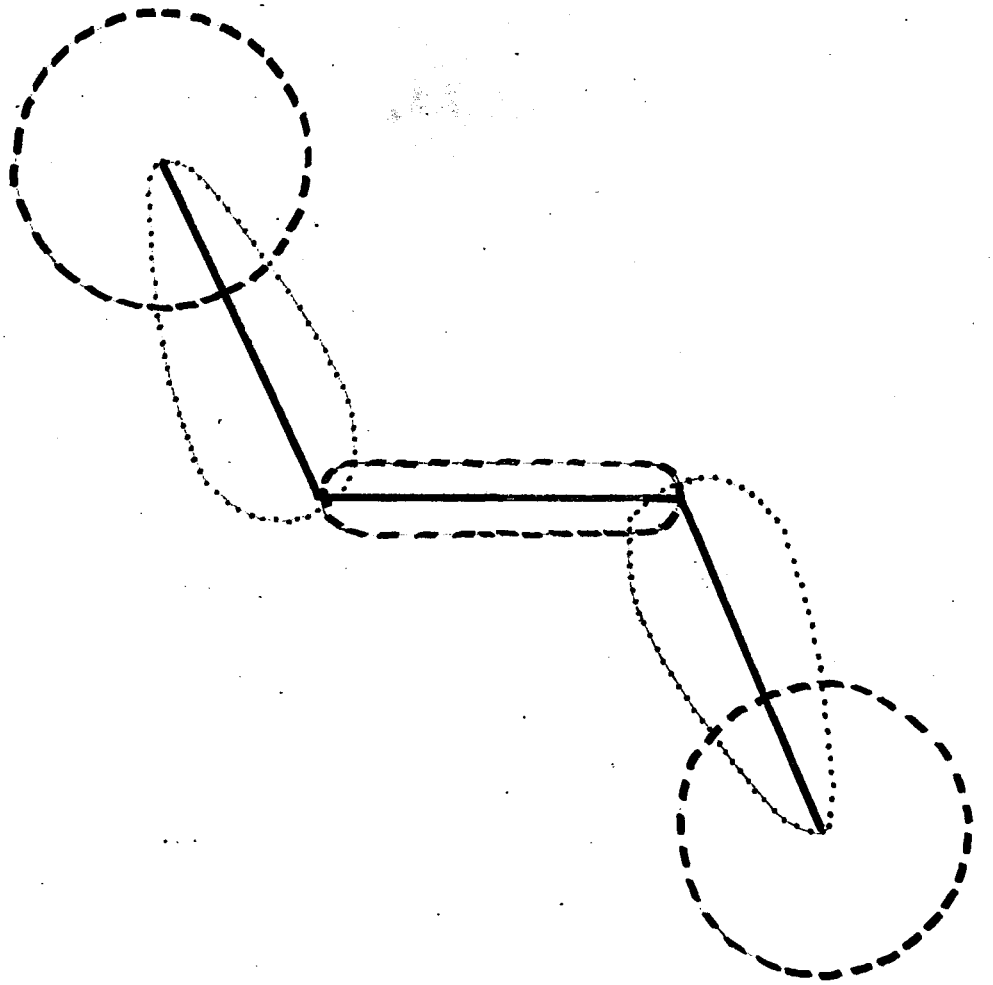


——— denotes a one-electron bond containing a α electron

..... denotes a one-electron bond containing a β electron

Figure VII-D

The representation of the NPSO -variation 'A' - for the trans butadiene ion.



denotes a one-electron bond containing a α electron

denotes a one-electron bond containing a β electron

Figure VII-E

The representation of the symmetrical NPSO wavefunction for the trans butadiene ion.

and

$$\psi_{II} = A\left|\chi_4(1)\alpha(1)\ (\chi_3+k\chi_2)(2)\alpha(2)\right. \qquad \text{..7-10}$$
$$\left.\chi_1(3)\alpha(3)\ (\chi_4+k\chi_3)(4)\beta(4)\ (\chi_1+k\chi_2)(5)\beta(5)\right|$$

for the symmetricl NPSO

$$\psi_I = A\left|\chi_1(1)\alpha(1)\ (\chi_2+\chi_3)(2)\alpha(2)\ \chi_4(3)\alpha(3)\right. \qquad \text{..7-11}$$
$$\left.(\chi_1+\chi_2 k)(4)\beta(4)\ (\chi_3 k+\chi_4)(5)\beta(5)\right|$$

and

$$\psi_{II} = A\left|\chi_1(1)\alpha(1)\ (\chi_2+\chi_3)(2)\alpha(2)\ \chi_4(3)\alpha(3)\right. \qquad \text{..7-12}$$
$$\left.(\chi_1+k\chi_2)(4)\beta(4)\ (\chi_4+k\chi_3)(5)\beta(5)\right|$$

Here ψ_I equals ψ_{II}.

Pauncz (110) discussed in some detail the merits of the two NPSO wavefunctions labelled, in his notation, variant 'A' and variant 'B'; he concludes that although in general variant 'B' is best, but also notes that on some occasions variant 'A' is superior. Here variant 'A' should be superior, since the repulsions can be described as: one small repulsion, on atom 2, comparable to those on and around atoms 2 and 3 in variant 'B'; two slightly larger ones, on and around atoms 1 and 4, comparable to that of atom 1 in variant 'B', and one more repulsion on atom 3, also small.

The result of the unprojected NPSO calculations are given in table VII-2b. Use of the variant 'A' NPSO wavefunction improves the energy sufficiently so that the unprojected NPSO energy is now lower than the MO energy.

Logically, it may seem that the symmetrical NPSO wavefunction should give the lowest energy. Empirically it is not easy to make such a statement, because it will depend on the relative sizes of the repulsions on atoms 2 and 3. Both the variant 'A' and the symmetrical NPSO wavefunctions (if the minimum k values are equal) will have similar $\alpha-\beta$ repulsions on and around atoms 2 and 4.

The results of the energy calculations using the symmetrical NPSO wavefunction are given in table VII-2b. Since both the wavefunctions, NPSO-A and symmetrical NPSO, have similar energy minima, at similar k value, we can only conclude that the $\alpha-\beta$ repulsions on atoms 2 and 3 in variant 'A' wavefunction balance those in the symmetrical wavefunction.

For all three wavefunctions spin density calculations were performed. The results, along with those of Amos and Snyder,(42), for a single determinant are given in table VII-2c.

Unlike the pentadienyl radical results, where the wavefunction that gave minimum energy gave spin densities comparable to those of Amos and Snyder, for the butadiene negative ion such a wavefunction gives spin densities in very poor agreement - there is even a sign difference. However ths spin density calculation with the variant 'B' NPSO wavefunction are in reasonable agreement with those of Amos and Snyder. This may tend to indicate that a good wavefunction - by energy criteria, is not such a good one, when judged by other standards. (Criteria for "good"

wavefunctions are discussed by Kutzelnigg and Smith,(111). Other workers have found it necessary to reminimise the wavefunction for calculation of physical quantities other than energy.)

B: Cis Butadiene Negative Ion.

As with the trans butadiene negative ion calculations, we assumed the geometry for the cis butadiene ion to be regular. See figure VII-F for the geometry and numbering scheme.

The integrals used were calculated by the Ruedenberg approximations and the Mulliken approximation. The integrals are given in table VII-2d.

We performed calculations using three types of unprojected NPSO wavefunctions. For all cases:

$$\psi_T = \psi_I + \psi_{II} \qquad ..7\text{-}7$$

The variant 'A' NPSO wavefunction has

$$\psi_I = A\left|\chi_1(1)\alpha(1)\ (\chi_2+k\chi_3)(2)\alpha(2)\ \chi_4(3)\alpha(3)\ (\chi_1+k\chi_2)(4)\beta(4)\ (\chi_4+k\chi_3)(5)\beta(5)\right| \qquad ..7\text{-}13$$

and

$$\psi_{II} = A\left|\chi_4(1)\alpha(1)\ (\chi_3+k\chi_2)(3)\alpha(3)\ \chi_1(3)\alpha(3)\ (\chi_4+k\chi_3)(4)\beta(4)\ (\chi_1+k\chi_2)(5)\beta(5)\right| \qquad 7\text{-}14$$

The variant 'B' NPSO wavefunction has

$$\psi_I = A\left|\chi_1(1)\alpha(1)\ (\chi_2+k\chi_3)(2)\alpha(2)\ \chi_4(3)\alpha(3)\ (\chi_1+k\chi_2)(4)\beta(4)\ (\chi_3+k\chi_4)(5)\beta(5)\right| \qquad ..7\text{-}15$$

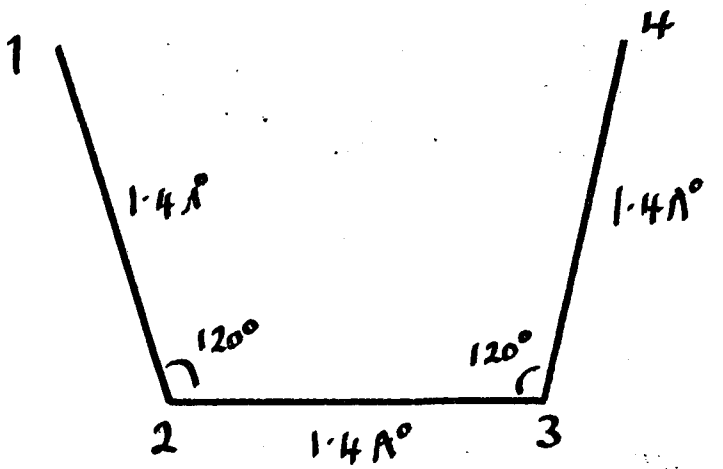


Figure VII-F

The geometry and numbering scheme for the cis butadiene ion.

Integral values for the cis butadiene ion.

element	coulomb integral	overlap integral	matrix element of the Hamiltonian.
11	17.22703	1.0	-41.21988
22	17.22703	1.0	-47.14124
12	9.02847	0.24682	-13.31621
13	5.65114	0.03470	-1.34984
14	4.94987	0.01545	-0.56951
23			-13.81955

Table VII-2d.

and

$$\psi_{II} = A\left|\chi_4(1)\alpha(1)\quad(\chi_3+k\chi_2)(2)\alpha(2)\quad\chi_1(3)\alpha(3)\quad(\chi_4+\chi_3 k)(4)\beta(4)\quad(\chi_2+k\chi_1)(5)\beta(5)\right| \quad ..7\text{-}16$$

The wavefunction with a symmetrical centre bond has:

$$\psi_I = A\left|\chi_1(1)\alpha(1)\quad(\chi_2+\chi_3)(2)\alpha(2)\quad\chi_4(3)\alpha(3)\quad(\chi_1+k\chi_2)(4)\beta(4)\quad(\chi_4+k\chi_3)(5)\beta(5)\right| \quad ..7\text{-}17$$

and

$$\psi_{II} = A\left|\chi_4(1)\alpha(1)\quad(\chi_3+\chi_2)(2)\alpha(2)\quad\chi_1(3)\alpha(3)\quad(\chi_4+k\chi_3)(4)\beta(4)\quad(\chi_1+k\chi_2)(5)\beta(5)\right| \quad ..7\text{-}18$$

The results of the energy calculations, including the MO energy are given in table VII-2e. These results show the same trend as those for the trans ion. The variant 'B' NPSO has a higher energy than the MO energy; whereas the variant 'A' NPSO wavefunction, and that with a symmetrical centre bond gave similar lowerings from the MO energy. Again the spin density results, table VII-2f, show that the variant 'B' NPSO wavefunction gives the most reasonable spin densities.

It is perhaps of interest to note that for both the MO and the unprojected NPSO wavefunction the cis butadiene ion appears to have a lower energy than that of the trans ion. The same problem has been observed previously,(114), and also with calculations for the cis and trans molecules,(115). Presumably the nuclear contribution to the total energy is greater

Results of the energy calculations for the cis butadiene ion.

all results are quoted in e.V.

method.	energy	k
MO	-140.96665 e.V.	
NPSO-B	-139.95795 e.V.	2.77
NPSO-A	-141.38767 e.V.	2.642
NPSO-symmetrical	-141.38766 e.V.	2.64

Table VII-2e

Results of the spin density calculations for the cis butadiene ion.

method	atom no.	1	2
Amos and Snyder[1]		0.475	0.025
NPSO-A		0.940	-0.233
NPSO-B		0.555	0.024
NPSO-symmetrical		0.921	-0.357

Table VII-2f.

[1] reference 42 .

for the cis ion than the trans.

In general altering the geometry leads to no improvement in the results - whether CI of SCF methods are used,(113); hence assumed geometry cannot explain the discrepancy.

VII.4: Naphthalene Negative Ion.

The geometry of the naphthalene negative ion, as used in these calculations, is shown in figure VII-G. It is after Pauncz and Silberman,(75). Their integrals were also used, see table VII-3a.

The NPSO wavefunction was initially set up as:

$$\psi_I = A\left|\begin{array}{cc}(\chi_1+k\chi_2)(1)\alpha(1) & (\chi_3+k\chi_4)(2)\alpha(2)\\ (\chi_6+k\chi_7)(3)\alpha(3) & (\chi_8+k\chi_9)(4)\alpha(4)\\ (\chi_9+k\chi_{10})(5)\alpha(5) & (\chi_{10}+k\chi_5)(6)\alpha(6)\\ (\chi_2+\chi_3 k)(7)\beta(7) & (\chi_4+k\chi_{10})(8)\beta(8)\\ (\chi_5+k\chi_6)(9)\beta(9) & (\chi_9+k\chi_1)(10)\beta(10)\\ & (\chi_7+k\chi_8)(11)\beta(11)\end{array}\right| \quad ..7\text{-}19$$

Again the symmetry projection operator for the D_{2h} point group must be applied to equation 7-19, to give:

$$\psi_T = \psi_I + \psi_{II} - \psi_{III} - \psi_{IV} \quad ..7\text{-}20$$

where

$$\psi_{II} = A\left|\begin{array}{cc}(\chi_1+k\chi_9)(1)\alpha(1) & (\chi_3+k\chi_2)(2)\alpha(2)\\ (\chi_6+k\chi_5)(3)\alpha(3) & (\chi_8+k\chi_7)(4)\alpha(4)\\ (\chi_{10}+k\chi_4)(5)\alpha(5) & (\chi_9+k\chi_{10})(6)\alpha(6)\\ (\chi_7+\chi_6 k)(1)\beta(7) & (\chi_5+k\chi_{10})(8)\beta(8)\\ (\chi_4+k\chi_3)(9)\beta(9) & (\chi_2+k\chi_1)(10)\beta(10)\\ & (\chi_9+k\chi_8)(11)\beta(11)\end{array}\right| \quad ..7\text{-}21$$

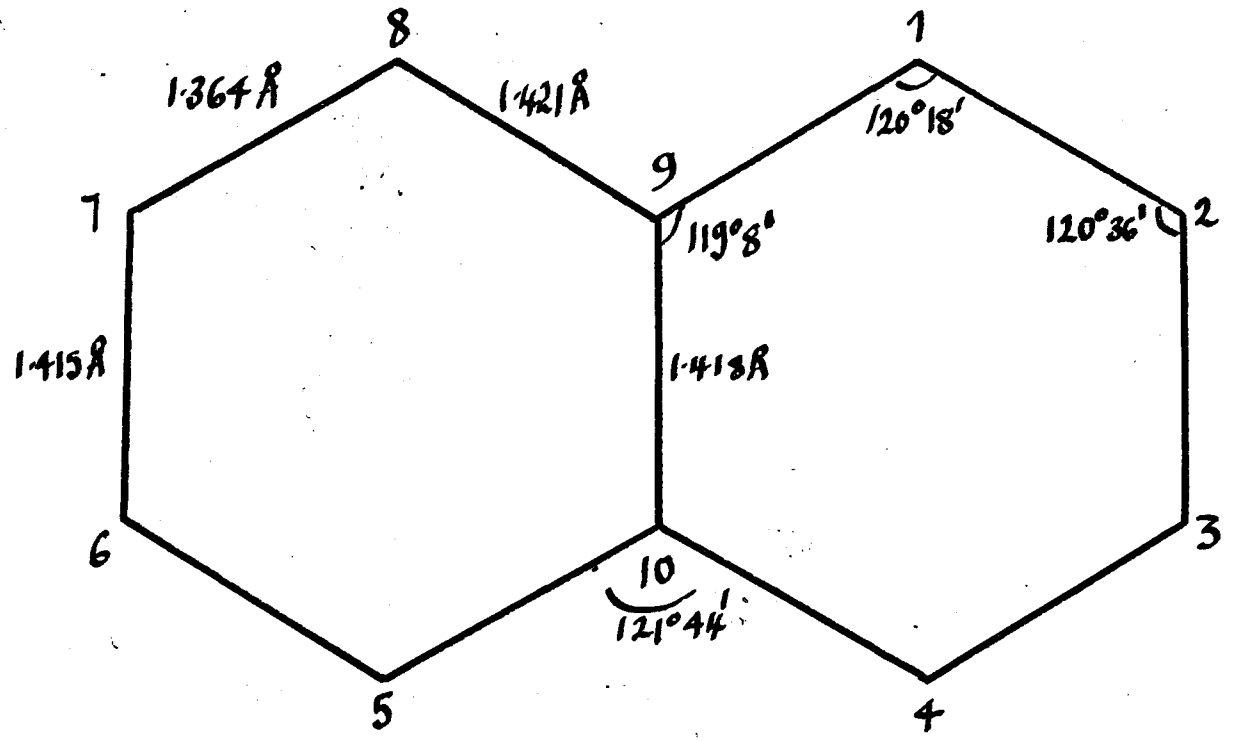


Figure VII-G

The geometry and numbering scheme of the naphthalene negative ion.

Integral values for naphthalene negative ion.[1]

element	coulomb integral	overlap integral	matrix element of the Hamiltoni
11	17.22895	1.0	-74.34875
21	9.21100	0.26199	-21.38680
22	17.22895	1.0	-70.97841
31	5.67494	0.03550	-2.35430
32	8.95552	0.24067	-19.15051
41	4.94385	0.01531	-1.04162
51	3.76271	0.00177	-0.12003
52	3.35407	0.00056	-0.03714
53	3.78695	0.00187	-0.12420
54	5.53083	0.03069	-2.08729
61	3.35407	0.00056	-0.03714
62	2.82798	0.00007	-0.00481
63	2.94449	0.00012	-0.00804
64	3.78695	0.00187	-0.12420
91	8.92621	0.23826	-20.76953
92	5.67494	0.03550	-2.50452
93	4.95371	0.01552	-1.09471
94	5.60304	0.03305	-2.38769
99	17.22895	1.0	-84.13052
10,9	8.94085	0.23946	-21.89262

[1] reference 75.

Table VII-3a.

$$\psi_{III} = A\,|\,(\chi_4 + k\chi_3)(1)\alpha(1)\ (\chi_2 + k\chi_1)(2)\alpha(2)$$
$$(\chi_9 + k\chi_8)(3)\alpha(3)\ \ (\chi_7 + k\chi_6)(4)\alpha(4)$$
$$(\chi_5 + k\chi_{10})(5)\alpha(5)\ \ (\chi_{10} + k\chi_9)(6)\alpha(6)$$
$$(\chi_3 + k\chi_2)(7)\beta(7)\ \ (\chi_1 + k\chi_9)(8)\beta(8)$$
$$(\chi_8 + k\chi_7)(9)\beta(9)\ \ (\chi_6 + k\chi_5)(10)\beta(10)$$
$$(\chi_{10} + k\chi_4)(11)\beta(11)\ |. \qquad ..7\text{-}22$$

and

$$\psi_{IV} = A\,|\,(\chi_5 + k\chi_6)(1)\alpha(1)\ \ (\chi_1 + k\chi_8)(2)\alpha(2)$$
$$(\chi_9 + k\chi_1)(3)\alpha(3)\ \ (\chi_4 + k\chi_{10})(4)\alpha(4)$$
$$(\chi_2 + k\chi_3)(5)\alpha(5)\ \ (\chi_{10} + k\chi_9)(6)\alpha(6)$$
$$(\chi_6 + k\chi_7)(7)\beta(7)\ \ (\chi_8 + k\chi_9)(8)\beta(8)$$
$$(\chi_1 + k\chi_2)(9)\beta(9)\ \ (\chi_3 + k\chi_4)(10)\beta(10)$$
$$(\chi_{10} + k\chi_5)(11)\beta(11)\ |. \qquad ..7\text{-}23$$

(Note: i) $\psi(k) \rightarrow \psi(1/k)$.

ii) ψ_{III} is ψ_I with α and β spins interchanged, except for the centre bond, (9 - 10)

and iii) ψ_{IV} is ψ_{II} with α and β spins interchanged, except for the centre bond.)

The results are given in table VII-3b, for both the NPSO and MO wavefunctions. It can be seen that the NPSO energy is in fact higher than the MO energy.

A similar calculation was performed, but with the (9 - 10) bond symmetrical. The NPSO wavefunction used was:

Results of the energy calculations for the naphthalene negative ion.

method	energy	k
MO	-504.39344 e.V.	
NPSO-A	-503.39625 e.V.	3.425
NPSO-symmetrical	-503,65201 e.V.	0.301

Table VII-3b.

Results of the spin density calculations for the naphthalene negative ion.

method	atom number					
	1	2	3	4	9	10
NPSO-symmetrical	0.916	-0.770	0.782	-0.707	0.222	0.790
Amos and[1] Snyder	0.262	0.026			-0.076	

Table VII-3c.

[1] regular geometry assumed.

$$\psi_T = \psi_I + \psi_{II} - \psi_{III} - \psi_{IV} \qquad ..7\text{-}20$$

where

$$\psi_I = A\,|\,(\chi_1+k\chi_2)(1)\alpha(1)\ (\chi_3+k\chi_4)(2)\alpha(2)\ (\chi_{10}+k\chi_5)(3)\alpha(3)\ (\chi_6+k\chi_7)(4)\alpha(4)\ (\chi_8+k\chi_9)(5)\alpha(5)\ (\chi_9+\chi_{10})(6)\alpha(6)\ (\chi_2+k\chi_3)(7)\beta(7)\ (\chi_4+k\chi_{10})(8)\beta(8)\ (\chi_5+k\chi_6)(9)\beta(9)\ (\chi_7+k\chi_8)(10)\beta(10)\ (\chi_9+k\chi_1)(11)\beta(11)\,| \qquad ..7\text{-}24$$

and

$$\psi_{II} = A\,|\,(\chi_1+k\chi_9)(1)\alpha(1)\ (\chi_3+k2)(2)\alpha(2)\ (\chi_{10}+k\chi_4)(3)\alpha(3)\ (\chi_6+k\chi_5)(4)\alpha(4)\ (\chi_8+k\chi_7)(5)\alpha(5)\ (\chi_9+\chi_{10})(6)\alpha(6)\ (\chi_4+k\chi_3)(7)\beta(7)\ (\chi_2+k\chi_1)(8)\beta(8)\ (\chi_9+k\chi_8)(9)\beta(9)\ (\chi_7+k\chi_6)(10)\beta(10)\ (\chi_5+k\chi_{10})(11)\beta(11)\,| \qquad ..7\text{-}25$$

and ψ_{III} is ψ_I with spins of all the electrons interchanged, except that of the electron in the (9-10) bond.

Here

$$\psi_{(k)} = \psi_{(1/k)}.$$

As can be seen from table VII-3b, the symmetrical unprojected NPSO energy is lower than the original energy - but it is still more than 0.5 e.V. above that of the MO wavefunction.

This may, at first sight, seem a short coming in the NPSO method, but again diagramatic representation of the wavefunction can perhaps

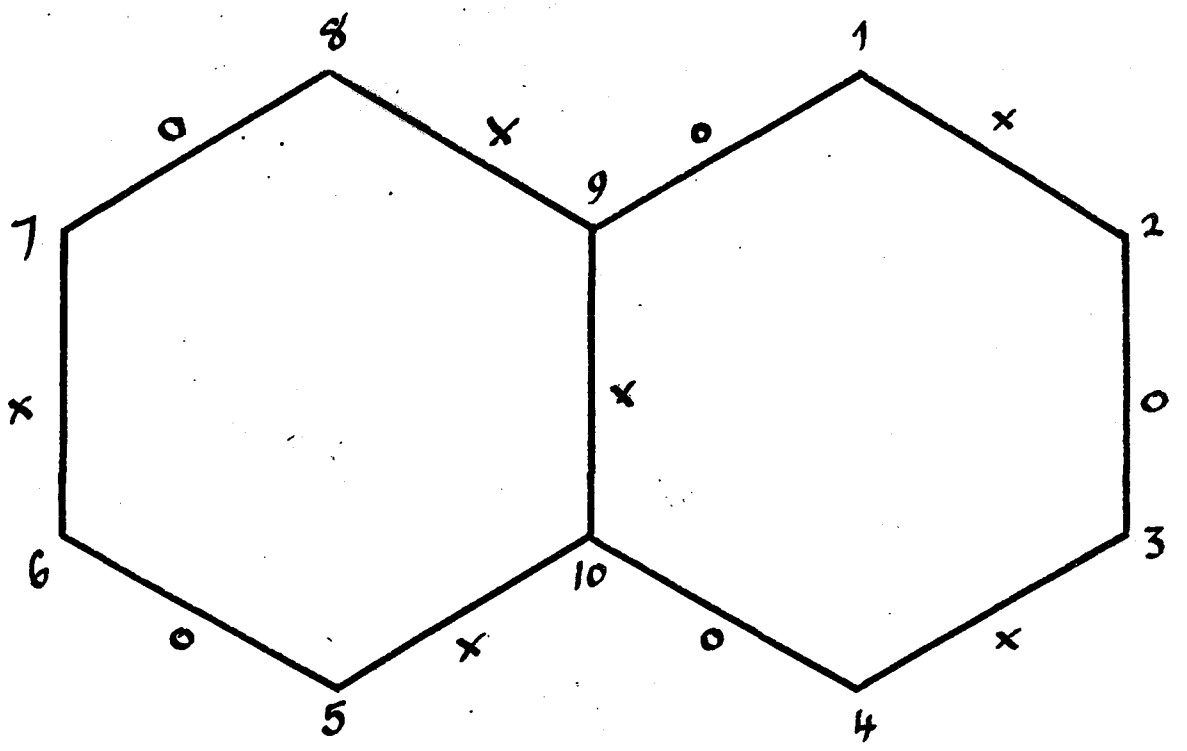
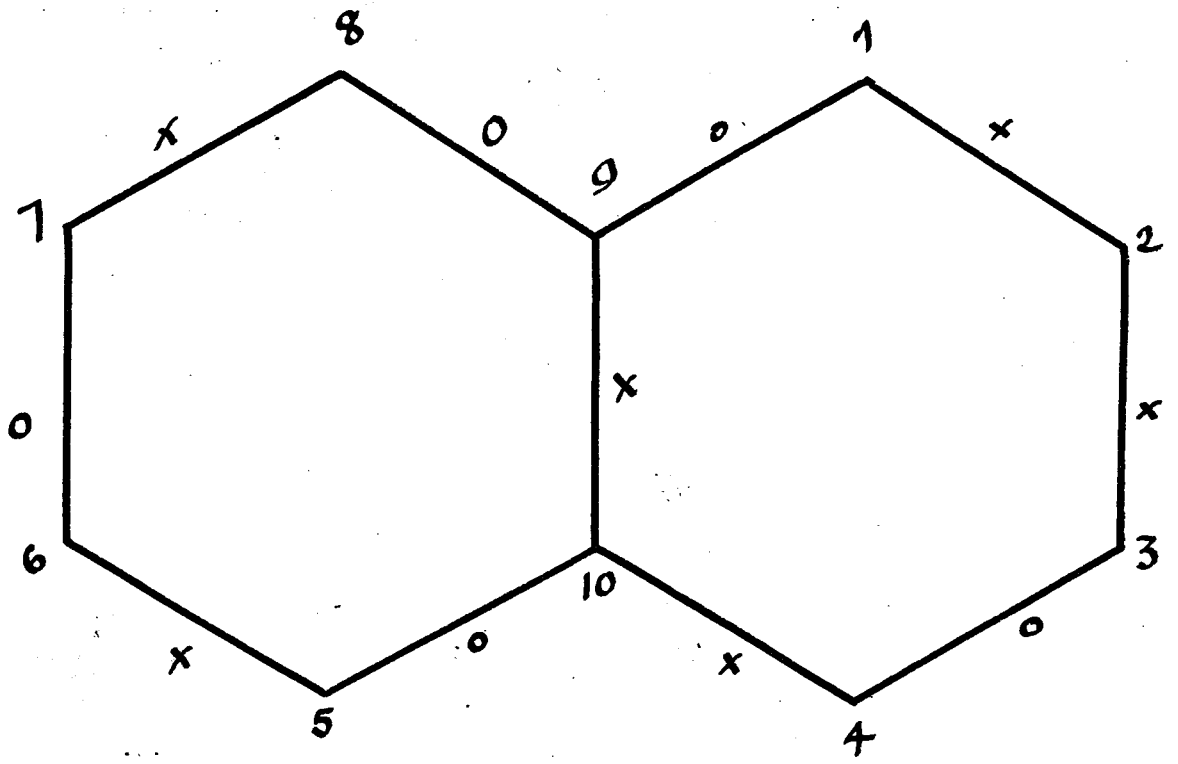


Figure VII-H (i) .. continued..

The arrangement of α and β spin electrons, in the naphthalene negative ion.

x denotes a one-electron orbital containing a α spin electron.

o denotes a one-electron orbital containing a β spin electron .



x denotes a one-electron orbital containing a α spin electron

o denotes a one-electron orbital containing a β spin electron.

Figure VII-H (ii)

The arrangement of α and β spin electrons, in the naphthalene negative ion.

give some indication as to why the NPSO wavefunction is less successful here than for naphthalene. (We shall show later that the same problems occur with the azulene negative ion.)

From figure VII-H (and many other feasible combinations of α and β electrons,) it is possible to see that always there will be two sets of parallel spin electrons in adjacent one-electron bonds; for example, figure VII-H (i) has α- electrons in pairs of bonds (8 - 9), (9 - 10) and (9 - 10), (10 - 5). This will always give a situation with high electron repulsions.

Although now we have an electron in the (9 - 10) , bridge bond, and so it is explicity included in the wavefunction, it is to the detriment of the NPSO wavefunction as a whole.

VII.5: Azulene Negative Ion.

With the azulene negative ion the bridge bond is included in the initial wavefunction, and again, as with the naphthalene negative ion, the results were disappointing.

The geometry of the azulene negative ion, and the numbering used, were those of the azulene molecule; see figureVII-J.

Again it is impossible to completely put electrons of the same spin into non-adjacent two centre bonds, see figure VII-K.

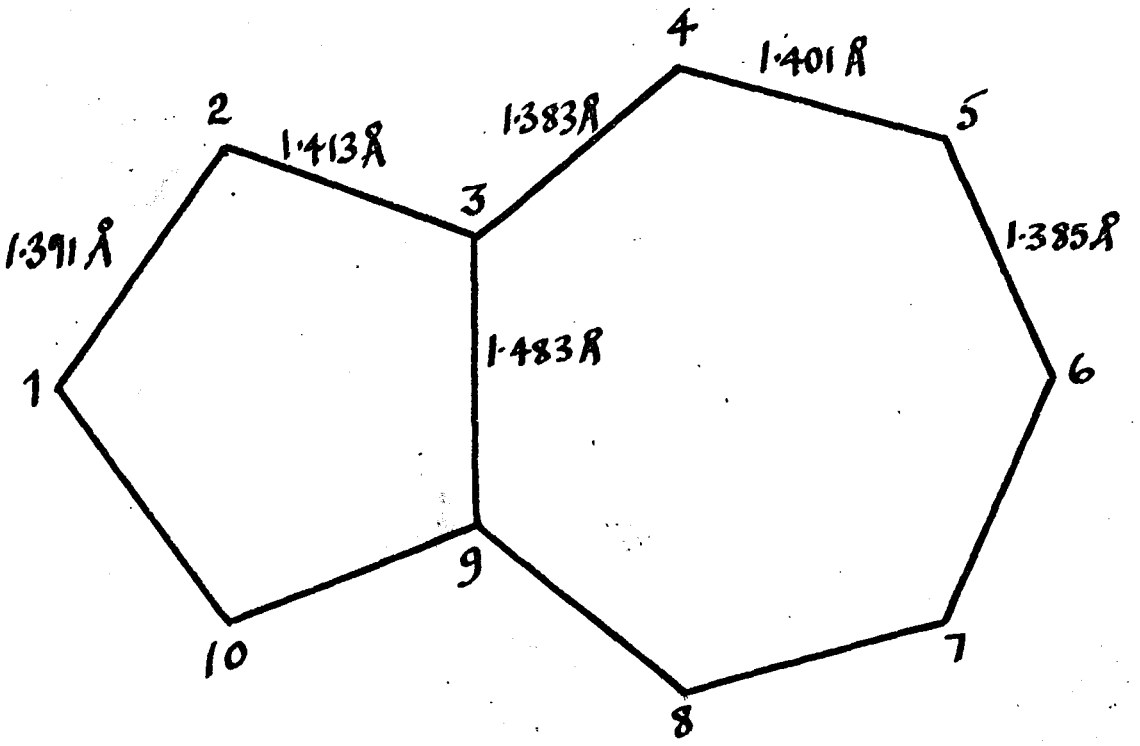
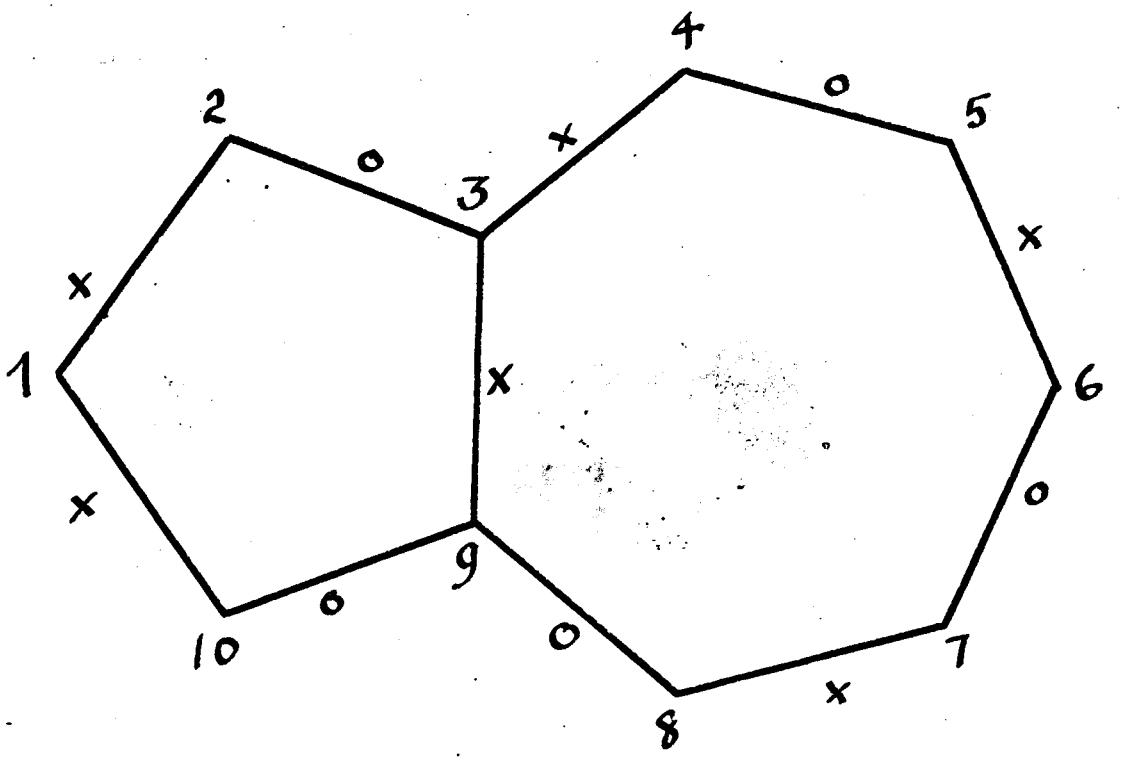


Figure VII-J

The geometry and numbering of the azulene negative ion.



x denotes a one-electron bond containing a α- spin electron

o denotes a one-electron bond containing a β- spin electron

Figure VII-K

The arrangement of α and β spin electrons in the azulene negative ion.

The NPSO wavefunction was set up by the application of the symmetry projection operator for the C_{2v} point group on the wavefunction $\psi_{,}$,

$$\psi_T = \psi_I + \psi_{II} \qquad \text{..7-26}$$

$$\psi_I = A\Big|\begin{matrix}(\chi_1 + k\chi_2)(1)\alpha(1) & (\chi_3 + k\chi_4)(2)\alpha(2) \\ (\chi_5 + k\chi_6)(3)\alpha(3) & (\chi_7 + k\chi_8)(4)\alpha(4) \\ (\chi_9 + k\chi_{10})(5)\alpha(5) & (\chi_3 + \chi_9)(6)\alpha(6) \\ (\chi_2 + k\chi_3)(7)\beta(7) & (\chi_4 + k\chi_5)(8)\beta(8) \\ (\chi_6 + k\chi_7)(9)\beta(9) & (\chi_8 + k\chi_9)(10)\beta(10) \\ (\chi_{10} + k\chi_1)(11)\beta(11) & \end{matrix}\Big| \qquad \text{..7-27}$$

$$\psi_{II} = A\Big|\begin{matrix}(\chi_1 + k\chi_{10})(1)\alpha(1) & (\chi_4 + k\chi_8)(2)\alpha(2) \\ (\chi_7 + k\chi_6)(3)\alpha(3) & (\chi_5 + k\chi_4)(4)\alpha(4) \\ (\chi_3 + k\chi_2)(5)\alpha(5) & (\chi_3 + \chi_9)(6)\alpha(6) \\ (\chi_{10} + k\chi_9)(7)\alpha(7) & (\chi_8 + k\chi_7)(8)\alpha(8) \\ (\chi_6 + k\chi_5)(9)\alpha(9) & (\chi_4 + k\chi_3)(10)\alpha(10) \\ (\chi_2 + k\chi_1)(11)\alpha(11). & \end{matrix}\Big| \qquad \text{..7-28}$$

Here $\psi(k) \neq \psi(1/k)$.

Results of the energy calculations for the azulene negative ion.

method	energy	k
MO	-502.20166 e.V.	
NPSO-symmetrical	-496.92216 e.V.	4.7

Table VII-4a.

Results of the spin density calculations for the azulene negative ion.

method	atom number									
	1	2	3	4	5	6	7	8	9	10
Amos and Snyder[1]	-0.011	0.118		0.313	-0.178	0.434			0.099	
NPSO	-0.952	0.907	-0.423	0.909	-0.848	0.846	-0.847	0.90	-0.114	0.261

Table VII-4b.

[1] regular geometry assumed.

The bridge bond was symmetrical. Note also that interchanges of spin in ψ_{I} and ψ_{II} need not be included.

The MO energy and the unprojected energy are given in table VII.-4a. It can be seen that the NPSO wavefunction fails to lower the energy below that of the MO wavefunction.

VII.6:

Throughout the calculations the unprojected NPSO method was used, with theoretical integrals. Although the inclusion of full spin projection, or even an approximation to it, should improve the results of the NPSO method, it is doubtful whether even this would give much better results for the azulene and naphthalene negative ions.

VIII:THE FULLY SPIN PROJECTED NPSO WAVEFUNCTION.

VIII:1:Introduction.

From previous calculations it seems reasonable to assume that the NPSO wavefunction will give a good energy lowering from the MO energy, for molecules. For medium sized ring systems, such as benzene, naphthalene and azulene, the results are promising. The unprojected energies, as expected are not as good as those from wavefunctions which have some allowance for spin projection. By increasing the allowance for spin projection the energies improve; any improvement in the wavefunction should lead to an improvement in the spin density results. Annihilation as an approximation, when calculating spin density has already been criticised,(39). It would thus be of great interest if a practical method of fully projecting the NPSO wavefunction could be found.

Here we propose such a method. It is, in fact, a synthesis of the AMO method and the NPSO method. Pauncz(149) has discussed the choice of molecular orbitals to be used as starting orbitals in the AMO method. He showed that, especially in the case of non-alternant systems, the choice of starting orbitals is quite critical. By using optimised molecular orbitals as the initial molecular orbitals, the azulene ground state energy was reduced by over 2 e.V. , from that of the one-parameter AMO calculation. We propose to use the natural orbitals (NO) of the first order density matrix, (FODM) of the NPSO wavefunction; but first we shall discuss density matrix methods in general.

VIII.2: Density Matrix Theory.

It has been suggested that (120) the problem of finding an approximate ground state wavefunction for a many particle system may be simplified by the use of density matrices.

The N-electron density matrix is defined as (122)

$$\rho(x_1, x_2, \ldots x_n \mid x_1', x_2' \ldots x_n') = \psi(x_1, x_2, \ldots x_n)\, \psi^*(x_1', x_2', \ldots x_n') \quad ..8\text{-}1$$

where x_i denotes both the co-ordinates of position and spin of the electron, i .

Since the density matrix was first introduced by Von Neuman,(117), through statistical mechanics, we must expect it to have physical significance. Thus

$$\psi(x_1, \ldots x_n)\, \psi^*(x_1, \ldots x_n)\, dx_1 dx_2 \ldots dx_n = \rho(x_1, \ldots x_n \mid x_1, \ldots x_n)\, dx_1 \ldots dx_n \quad ..8\text{-}2$$

gives the probability of finding electron 1 in volume dx_1, electron 2 in the volume dx_2, ... and electron n in volume element dx_n.

$\rho(x_1, \ldots x_n \mid x_1, \ldots x_n)\, dx_1 dx_2 \ldots dx_n$ is just the diagonal element of the density matrix, multiplied by the volumes dx_1 to dx_n. The probability of electron 1 being in dx_1 and the other (n-1) electrons being anywhere is given by:-

$$dx_1 \int \psi(x_1 \ldots x_n)\, \psi^*(x_1 \ldots x_n)\, dx_2 \ldots dx_n \quad ..8\text{-}3$$

The probability of any electron being in the volume element

is n times this, because the electrons are indistinguishable; viz:-

$$N\, dx_1 \int \psi(x_1 \ldots x_n)\, \psi^*(x_1 \ldots x_n)\, dx_2 \ldots dx_n = \rho_1(x_1 | x_1')\, dx_1 \qquad \ldots 8\text{-}4$$

From this equation, 8-4, we define the reduced density matrices.

$\rho_p(x_1 \ldots x_p | x_1' \ldots x_p')$ here the density matrix is of order p.

Now $\rho_1(x_1 | x_1')$ is the first order density matrix,

$$\rho_1(x_1 | x_1') = N \int \psi(x_1 \ldots x_n)\, \psi^*(x_1' \ldots x_n)\, dx_2 \ldots dx_n \qquad \ldots 8\text{-}5$$

and similarly the second order density matrix $\rho_2(x_1 x_2 | x_1' x_2')$ is defined such that it determines the probability of two electrons being found simultaneously with co-ordinates x_1 and x_2 :

$$\rho_2(x_1 x_2 | x_1' x_2') = N(N-1) \int \psi(x_1, x_2 \ldots x_n)\, \psi^*(x_1', x_2' \ldots x_n)\, dx_3 \ldots dx_n \qquad \ldots 8\text{-}6$$

$$\int \rho_2(x_1 x_2 | x_1' x_2')\, dx_1\, dx_2 = \binom{N}{2} \qquad \ldots 8\text{-}7$$

The FODM can be obtained from the second order density matrix by

$$\rho_1(x_1 | x_1') = \frac{2}{N-1} \int \rho_2(x_1 x_2 | x_1' x_2')\, dx_2 \qquad \ldots 8\text{-}8$$

Density matrices possess the following properties,(119):-

i) They are Hermitian.

$$\rho_2(x_1 x_2 | x_1' x_2') = \rho_2^*(x_1' x_2' | x_1 x_2) \quad ..8\text{-}9$$

ii) They are antisymmetric with respect to interchange of variables.

$$\rho_2(x_2' x_1' | x_1 x_2) = -\rho_2(x_1' x_2' | x_1 x_2) \quad ..8\text{-}10$$

iii)They can be written in terms of orbitals as,(122),

$$\rho(x|x') = \sum_k \sum_l \rho_{kl}\, \psi_k(x)\, \psi_l^*(x') \quad ..8\text{-}11$$

and

iv)We can write (122) the expectation value of any operator F as $\langle F \rangle$,

$$\langle F \rangle = \int \psi^* F \psi \, d\tau \quad ..8\text{-}12$$

$$= \int_{x'=x} F\, \rho(x:x')\, dx \quad ..8\text{-}13$$

Here the operator F operates only on x', and after the operation x' is set equal to x, before the integration is performed.

For a system containing only two particle operators, we thus need only the second order density matrix to give the expectation value of the operators.

Consider the Hamiltonian operator, H, this can be

written in terms of one and two electron operators as

$$H = \sum_i h(i) + \tfrac{1}{2} \sum_{i<j} g(i,j) \qquad \text{..8-14}$$

The expectation value of the Hamiltonian, $\langle H \rangle$, gives

$$E = \int_{x_1'=x_1} h(1)\, \rho_1(x_1 : x_1')\, dx_1 + \int_{\substack{x_1'=x_1 \\ x_2'=x_2}} g(1,2)\, \rho_2(x_1 x_2 : x_1' x_2')\, dx_1\, dx_2 \qquad \text{..8-15}$$

When dealing with spin-free operators we can reduce the density matrices further, to give spinless density matrices, $\rho_p^s(r_1 \ldots r_p : r_1' \ldots r_p')$.

Here p is the order of the spinless density matrix, and r denotes position co-ordinates, only.

The first and second order spinless density matrices are defined by

$$\rho_1^s(r_1 : r_1') = \int_{s_1'=s} \rho_1(x_1 : x_1')\, ds_1 \qquad \text{..8-16}$$

that is, as the FODM integrated over spin.

$\rho_1^s(r_1 : r_1')$ gives the probability per unit volume of finding an electron in dr_1, with co-ordinates r_1, without regard to spin.

$$\rho_2^s(r_1 r_2 : r_1' r_2') = \int_{\substack{s_1'=s_1 \\ s_2'=s_2}} \rho_2(x_1 x_2 : x_1' x_2')\, ds_1\, ds_2 \qquad \text{..8-17}$$

From the definitions of the spinless density matrices we can give the expectation value of the spinless Hamiltonian, H, (equation 1-2), as

$$E = \langle H \rangle$$

$$= \int_{r_1'=r_1} h(1)\, \rho_1^S(r_1 : r_1')\, dr_1$$

$$+ \int_{\substack{r_1'=r_1 \\ r_2'=r_2}} g(1,2)\, \rho_2^S(r_1, r_2 : r_1' r_2')\, dr_1\, dr_2 \qquad \text{..8-18}$$

We can also express spin density in terms of these spinless density matric es. The first order spinless density matricies can be separated into terms due to α- spin and terms due to β- spin. That

$$\rho^S(r_1 : r_1') = \rho_1^{\alpha}(r_1 : r_1') + \rho_1^{\beta}(r_1 : r_1') \qquad \text{..8-19}$$

can be deduced from the calculation of $\rho_1(x_1 : x_1')$ and its integration, (118), (123).

The electron density is now the sum of two parts - the spin density is defined as the difference of these parts.

$$S_1(r_1 : r_1') = \rho_1^{\alpha}(r_1 : r_1') - \rho_1^{\beta}(r_1 : r_1') \qquad \text{..8-20}$$

when $r_1' = r_1$.

VIII.3: Density Matrix Calculations.

" It is well known that reduced density matric es provide a good way of interpreting many-electron wave-functions. ..... The density matrix is a particularly useful way of comparing functions of different types. It may be possible on the basis of a density matrix analysis to make rather general statements about the

description of any wavefunction of a particular type can make, as in the case of a spin projected DODS single determinant."(121).

With this in mind the first order density matrices were calculated for some of the systems so far studied; those with bridge bonds, namely azulene, phenanthrene and anthracene. Löwdin,(122), gave formulae from which it is possible to calculate the FODM. If the initial wavefunction $\Psi(x_1, x_2, \ldots x_n)$ is a determinant of spin orbitals $\phi_1, \phi_2, \ldots \phi_n$, which are not necessarily orthogonal, we define $\rho_1(x_1 : x_1')$ as

$$\rho_1(x_1 : x_1') = \sum_k \sum_l \phi_k^*(x_1)\, \phi_l(x_2)\, \delta^{-1}(lk) \qquad \ldots 8\text{-}21$$

where

$$\delta^{-1}(kl) = \frac{D(kl)}{D} \qquad \ldots 8\text{-}22$$

and

$$D = \det |\delta(kl)| \qquad \ldots 8\text{-}23$$

$$\delta(kl) = \int \phi_k^*(x_1)\, \phi_l(x_1)\, dx_1 \qquad \ldots 8\text{-}24$$

i)Azulene.

The results of the calculation of the first order density matrix for the unprojected NPSO wavefunction for azulene are in table VIII-1. The AMO density matrix was also calculated, using equations 6.33,6.34,6.35 and 6.31 from Pauncz (67).

First order density matrix for azulene.

element	unprojected NPSO (k = 0.2555)	optimised AMO
11	0.9021	0.8516
22	0.9057	0.9626
33	0.9354	0.8308
44	0.8989	0.7934
55	0.9001	0.8481
66	0.8964	0.8040
12	0.2098	0.2934
23	0.2190	0.2743
34	0.2155	0.3242
45	0.2125	0.3450
56	0.2113	0.3008
39	- 0.1693	0.o713

table VIII-1.

$$\rho_1(x_1/x_1') = \sum_k (n_k \psi_k(x_1) \psi_k^*(x_1') + n_{\bar{k}} \psi_{\bar{k}}(x_1) \psi_{\bar{k}}^*(x_1'))$$

..8-25

where n_k and $n_{\bar{k}}$ are given by

$$n_k = 2 - F_k(\lambda_1 \ldots \lambda_n) \qquad ..8\text{-}26$$

$$n_{\bar{k}} = F_k(\lambda_1 \ldots \lambda_n) \qquad ..8\text{-}27$$

and

$$F_k = (1-\lambda_k)\left[1 - \lambda_k \left(1 + \frac{\lambda_k}{\Lambda_0}\right) \frac{d\Lambda_0}{dx_k}\right] \qquad ..8\text{-}28$$

The λ_k and Λ_0 are defined as previously,(chapter III). There appears to be some confusion between the values quoted in Pauncz's paper,(71), and those in his book,(74). Comparing the values of λ and the occupation numbers lead us to believe that the correct λ's were those in table 7-12, reference 71 , viz:-

0.8992 0.8541 0.8536 0.5064 0.5467

The AMO density matrix is given, along with that for the NPSO wavefunction, in table VIII-1.

Lack of definite inclusion of the (3 - 9) bond, (discussed in chapter IV) in the NPSO wavefunction is shown by the negative, antibonding, sign in the NPSO density matrix for the (3 - 9) element.

ii) Anthracene and Phenanthrene.

For both molecules the first order density matrices were calculated from Pauncz's formulae.

$$\rho_1(x_1;x_1') = \sum_k \left[a_k(x_1)\, a_k^*(x_1') + a_{\bar{k}}(x_1)\, a_{\bar{k}}^*(x_1') \right]$$

$$+ \sum_k{}' \lambda_k \frac{\partial \Lambda_0}{\partial x_k} \Big\{ \left[a_k(x_1)\, a_{\bar{k}}^*(x_1') + a_{\bar{k}}(x_1)\, a_k^*(x_1') \right] +$$

$$\lambda_k \left(a_{\bar{k}}(x_1)\, a_k^*(x_1) + a_k(x_1) a_{\bar{k}}^*(x_1) \right) \Big\} \quad 8\text{-}29$$

By using SCF-MO's as the starting orbitals for the AMO calculation, the FODM was also calculated for the SCF-MO wavefunction.(The mixing parameter, λ , was set to zero.) The FODM was calculated for the unprojected NPSO wavefunction. The results are given in table VIII-2 for anthracene, and table VIII-3 for phenanthrene.

For both molecules the bridge bonds, (11 - 12) and (13 - 14), have negative elements in the NPSO density matrices. This reflects the neglect of these bonds in the wavefunction.

VIII.4: Natural Orbitals.

Natural spin orbitals were first defined by Löwdin,(11), from the diagonalisation of the FODM.[2] For a wavefunction, Ψ, a single Slater determinant of a complete orthonormal set of spin orbitals, ϕ_i, the FODM, (including spin), can be defined as,

[2] Similarly Natural spin geminals are obtained by the diagonalisation of the second order density matrix.

First order density matrix for anthracene.

element	SCF-MO	NPSO	AMO
11	0.7459	0.9397	0.7675
22	0.7741	0.9374	0.7943
99	0.6795	0.9411	0.7048
11,11	0.8473	0.9474	0.8666
12	0.6707	0.1321	0.6174
23	0.2566	0.1365	0.2274
4,12	0.2264	0.1393	0.1991
9,11	0.4658	0.1364	0.4242
11,12	0.3879	-0.0357	0.3510

table VIII-2.

First order density matrix for phenanthrene.

element	SCF-MO	NPSO	AMO
11	0.7206	0.9402	0.7367
22	0.7581	0.9381	0.7727
33	0.7577	0.9381	0.7723
44	0.7211	0.9404	0.7371
99	0.7413	0.9402	0.7566
11,11	0.8615	0.9466	0.8750
12,12	0.8379	0.9489	0.8524
12	0.5410	0.1345	0.5140
23	0.4352	0.1345	0.4076
34	0.5369	0.1345	0.5053
4,12	0.4188	0.1367	0.3914
9,10	0.6710	0.1343	0.6342
10,11	0.2347	0.1370	0.2145
1,11	0.4080	0.1368	0.3768
11,12	0.4340	-0.0370	0.4058

table VIII-3.

$$\rho_1(x_1|x_1') = \sum_i \sum_j \rho_{ij}\, \phi_i\, \phi_j^* = \rho_1 \qquad \text{..8-30}$$

Since ρ_1 is hermitian, the use of a unitary transformation can diagonalise ρ_1 ..

$$\underline{U}^{\dagger}\, \rho_1\, \underline{U} = \underline{n} \qquad \text{..8-31}$$

where n is a diagonal matrix.

Thus:-

$$\rho_1 = \underline{U}\, \underline{n}\, \underline{U}^{\dagger} \qquad \text{..8-32}$$

We can use the transform $\underline{U}$ to define new spin orbitals χ_k, such that

$$\chi_k = \sum_i \phi_i\, U_{ik} \qquad \text{..8-33}$$

Now the FODM, ρ_1, has the simple form

$$\rho_1(x_1 : x_1') = \sum_k n_k\, \chi_k(x_1)\, \chi_k^*(x_1') \qquad \text{..8-34}$$

Here the diagonal elements of n in equation 8-31, n_k, are called the occupation numbers. They represent the average number of electrons in each natural spin orbital, NSO, χ_k. The occupation numbers satisfy the following conditions.

$$\sum_k n_k = N \qquad \text{..8-35}$$

and

$$0 \leq n_k \leq 1$$

(For an orthonormal set of spin orbitals.)

The NSO are symmetry orbitals, (123), which are not in general localised orbitals, though localised orbitals can be constructed from them. They can be used to

give faster convergance in CI calculations, (124).

By analogy, the natural orbitals can be defined as eigenvectors of the spinless FODM. The relationship of the NSO to the natural orbitals (NO) can be stated as, (125), if m = 0, for the z-component of spin of the total wavefunction, the NSO will equal the NO multiplied by a spin factor, (α or β).

VIII.5:Fully Spin Projected NPSO Calculations.

i) Introduction.

Previous calculations using NPSO wavefunctions have been unable, because of the size of the computational problem, to include full spin projection of the wavefunction. It is thought that, although this lack of spin projection is not a great omission for energy calculations, it could greatly affect the spin density results, and hence account at least to some extent, for the poor benzyl spin density results . Here we suggest a method of performing fully spin projected calculations. The approach of this method differs from that of using a projection operator on a symmetry projected wavefunction - it is in fact a combination of both the previously used unprojected NPSO method and the AMO method. The projection of a single determinant, DODS, of alternant orbitals formed from the natural orbitals of the unprojected NPSO spinless FODM is calculated; the occupation numbers give the mixing parameter for the alternant orbitals.

ii) Theory

The spinless FODM, (equation 8-16), can be written in terms of the atomic orbital basis set, $\{\chi_i\}$,

$$\rho_1^S(r_1 : r_1') = \sum_i \sum_j \rho_{ij} \chi_i(r_1) \chi_j^*(r_1') \qquad ..8\text{-}36$$

Transforming the AO basis to an orthogonal atomic orbital, (OAO) set, $\{\chi_i^o\}$, means that the trace of ρ_1^S will be equal to n, the number of electrons. The AO's can be transformed to the OAO's, using for example, the method of Löwdin, (141),

$$\chi_i^o = \sum_j T_{ij} \chi_j \qquad ..8\text{-}37$$

where $\underline{T} = \underline{S}^{-\frac{1}{2}}$

and

$$S_{ij} = \int \chi_i \chi_j \, d\tau \qquad ..8\text{-}38$$

The FODM can now be expressed in the OAO basis;

$$\rho_1^S(r_1 : r_1') = \sum_i \sum_j \rho_{ij}^o \chi_i^o(r_1) \chi_j^{*o}(r_1') \qquad ..8\text{-}39$$

and it can be diagonalised to give the natural orbitals, $\{\phi_i^o\}$, in the OAO basis, such that

$$\rho_1^S(r_1 : r_1') = \sum_i N_i \phi_i^o(r_1) \phi_i^{*o}(r_1') \qquad ..8\text{-}40$$

The occupation numbers, N_i, now satisfy the relations

i) $$0 \leq N_i \leq 2$$

and

ii) $$\sum_i N_i = n \qquad ..8\text{-}41$$

and

iii) if the NO's are ordered by decreasing occupation numbers, it can be shown that, (143)

$$\tfrac{1}{2}\left[N_i + N_{n+1-i}\right] = 1 \qquad i = 1,2 \cdots \nu, \qquad \text{..8-42}$$

and

$$N_{\nu+j} = 1 \qquad j = 1, \ldots 2m \qquad \text{..8-43}$$

where

ν = number of β electrons, μ = number of α electrons,

and $m = \frac{1}{2}(\mu - \nu)$

Thus it is possible to form two sets of natural orbitals, (each set with ν members), having the property that every orbital of the first set is paired with an orbital in the second set. A third set - defined by equation 8-43 - has no pairing properties. Using these properties Harriman, (142), formed the CO, corresponding orbitals of Amos and Hall,(37), or the paired orbitals of Löwdin,(36), from the following relationships:-

if u_i and v_i are the paired or corresponding orbitals,

$$u_i = \cos\theta_i \phi_i^o + \sin\theta_i \phi_{n+1-i}^o \qquad \text{..8-44}$$

$$v_i = \cos\theta_i \phi_i^o - \sin\theta_i \phi_{n+1-i}^o \qquad i = 1 \ldots \nu \qquad \text{..8-45}$$

and

$$u_{\nu+j} = \phi_{\nu+j}^o \qquad j = 1 \cdots 2m \qquad \text{..8-46}$$

where

$$\cos 2\theta_i = \tfrac{1}{2}\left[N_i - N_{n+1-i}\right] \qquad \text{..8-47}$$

Since the corresponding orbitals satisfy equation 3-27, the energy of a DODS wavefunction of the type

$$\psi = A\left[u_1\alpha\, u_2\alpha\, u_3\alpha \cdots u_\mu\alpha\, v_1\beta \cdots v_\nu\beta\right] \qquad \text{..8-48}$$

can be calculated, after full spin projection, by the

method of Pauncz, for closed shell systems or Harris for open shell systems.

iii) Calculations.

We used the natural orbitals of the unprojected NPSO density matrix to form corresponding orbitals. These orbitals were used to form a Slater determinant within a DODS framework, and a wavefunction of the type given by equation 8-39 was formed. This was fully spin projected to give

$$\psi = O_S \, A \left| u_1(\alpha)\, u_{1'}(\alpha) \cdots v_1(\beta) \cdots \quad v_{\nu}(\beta) \right| \quad ..8\text{-}49$$

Before performing the calculations the corresponding orbitals were transformed back to the AO basis, $\{\chi_i\}$, since by this means transformation of the integrals to the OAO basis, $\{\chi_i^o\}$, can be avoided.

Throughout the calculations, the integrals used were those previously used, calculated by Ruedenberg's method, to facilitate comparision.

VIII.6: Applications of the Fully Spin Projected NPSO Method.

i) Anthracene and Phenanthrene.

The initial NPSO wavefunction used to calculate the density matrix was equation 5-2 for anthracene, and equation 5-6 for phenanthrene.

The energy minima are quoted in table VIII-4 and VIII-5, along with the AMO energy,(one-parameter calculation) and the previous best NPSO energy.

Results of the energy calculations for anthracene.

all energies are quoted in e.V.

method	energy	k
SCF-LCAO-MO	-777.2444 e.V.	
AMO	-777.3830 e.V.	
projected and unprojected NPSO	-782.0769 e.V.	0.2
fully spin projected NSPO	-783.6010 e.V.	0.274

table VIII-4

Results of the energy calculations for Phenanthrene.

all energies are quoted in e.V.

method	energy	k
SCF-LCAO-MO	-788.2206 e.V.	
AMO	-788.2891 e.V.	
projected and unprojected NPSO	-793.0594 e.V.	0.2
fully spin projected NPSO	-794.4813 e.V.	0.278

table VIII-5.

First order density matrix for anthracene.

element	fully spin projected NPSO
11	0.9248
22	0.9221
99	0.9262
11,11	0.9348
12	0.1625
23	0.1699
4,12	0.1736
9,11	0.1691
11,12	-0.0511

table VII-6

First order density matrix for phenanthrene.

element	fully spin projected NPSO
11	0.9272
22	0.9247
33	0.9246
44	0.9276
99	0.9272
11,11	0.9365
12,12	0.9396
12	0.1630
23	0.1628
34	0.1630
4,12	0.1665
9,10	0.1629
10,11	0.1675
1,11	0.1668
11,12	-0.0626

table VIII-7.

It can be seen that this fully spin projected method lowers the energy below that of the previous best NPSO energy, that from the projected and annihilated NPSO wavefunction.

The FODM's for this method are given in tables VIII-6 and VIII-7 . For both molecules the (11 -12) and (13 -14) elements are still negative, due to their non-inclusion in the wavefunction.

ii) Azulene.

The wavefunction, equation4-4 was used to calculate the density matrix from which the natural orbitals were formed. Since azulene is a non-alternant hydrocarbon, a similar pairing problem arose to that of Pauncz,(71). Pairing the NO's by occupation number to give the corresponding orbitals does not give a wavefunction with the correct symmetry properties. (That is it does not transform as one of the irreducible representations of the point group of the molecule.) Thus, after Pauncz,(71), we paired the NO's by symmetry. The following pairing scheme was used:-

(1, 10), (2, 8), (3, 9), (4, 6), (5, 7)

This pairing is probably not too drastic an alteration of the general method, since the orbitals, (ϕ_2^0 and ϕ_3^0) and (ϕ_4^0 and ϕ_5^0) have almost equal occupation numbers. viz:-

$N_2 = 1.717$, $N_3 = 1.709$; $N_4 = 1.333$, $N_5 = 1.305$.

The results, along with that of the previous AMO and best NPSO calculations are given in table VIII-8. Again the (3 - 9), bridge bond, element of the density

Results of the energy calculations for azulene.

all energies are quoted in e.V.

method	energy	k
SCF-LCAO-MO	-490.7623 e.V.	
AMO (5 parameters)	-493.1266 e.V.	
AMO (optimised)	-494.4050 e.V.	
Best NPSO	-495.8820 e.V.	0.228
fully spin projected NPSO	-496.4352 e.V.	0.284

table VIII-8

First order density matrix for azulene.

element	fully spin projected NPSO
11	0.9243
22	0.9313
33	0.9632
44	0.9277
55	0.9277
66	0.9180
12	0.1577
23	0.1606
34	0.16o2
45	0.1576
56	0.1595
39	-0.1771

table VIII-9.

matrix, (see table VIII-9), is antibonding,(negative). A good energy lowering was obtained.

iii) The Benzyl Radical.

The NPSO wavefunction used to form the density matrix was that of equation 6-3, NPSO-A wavefunction. The density matrix method lowers the energy from that previously obtained - see table VIII-10. The spin densities were calculated using Pauncz's formula, and the results are given in table VIII-11, along with those of the AMO method and Amos and Snyder's UHF method,(42). It can be seen that, although the spin densities are improved such that they are similar to those of the AMO method,they are still not in very good agreement with the experimental results.

iv) Semi-empirical Data.

Since the integrals used here have been questioned previously, and since the spin density results obtained using semi-empirical data seem to be more reasonable than those calculated from theoretical integrals,(42), we continued our work on the benzyl radical by using the parametrization recently suggested by Beveridge and Hinze,(139), that was found to be reasonably successful for calculating spin densities and energies of excited states. The one centre coulomb integral was set equal to $I_p - E_a$(133) coulomb integrals - all two centre ones - were calculated from equation 20, reference 139 ,all other multicentre two electron integrals

Results of the energy calculations for the benzyl radical.

all energies are quoted in e.V.

method	energy	k
RHF-MO	-305.6740 e.V.	
AMO	-308.6701 e.V.	
best NPSO	-309.5968 e.V.	4.85
fully spin projected NPSO	-309.7127 e.V.	4.62

table VIII-10.

Spin density results for the benzyl radical.

method	atom no.				
	1	2	3	4	7
AMO	-0.264	0.451	-0.270	0.455	0.537
Amos and Snyder [1]	-0.127	0.205	-0.105	0.175	0.752
NPSO (fully spin projected)	-0.262	0.454	-0.276	0.440	0.509
experimental hyperfine coupling constants (gauss). [2]		5.14	1.75	6.14	16.35

table VIII-11.

[1] reference 42

[2] reference 87

Beveridge and Hinze integral values for the benzyl radical.

element	coulomb integral	overlap integral	matrix element of the Hamiltonian.
11	11.13	1.0	-23.38473
12	6,78985	0.24682	-2.29102

all other integral values were set to zero.

table VIII-12.

were neglected. The overlap integrals, as suggested by Beveridge and Hinze, were used to calculate the beta values, but in the calculations we performed the original nearest neighbour overlap integrals were used, as these seemed more realistic. The data used is given in table VIII-12.

As a reference energy we performed an MO calculation - using eigenvectors of the complete overlap matrix as molecular orbitals. We calculated the energy using the fully spin projected NPSO method.

The results were:

Method	energy.	
MO	-109.4293 e.V.	
NPSO	-115.3258 e.V.	k = 0.0095

These results seem better than previous results using semi-empirical data; PPP data gave no energy lowering for the NPSO wavefunction from the MO one.

Again spin density calculations were performed; the results were not much improved; viz:-

1	2	3	4	7 . .	atom nos.
-0.165	0.2497	-0.161	0.250	0.266	

Since we have calculated the spin density using full spin projection, and semi-empirical data, with no improvement in the results, other reasons for the lack of success of the method must now be considered - e.g. assumed geometry.

v) Two variable parameters.

In a further attempt to calculate reasonable spin densities for the benzyl radical, we performed the fully spin projected calculation using the wavefunction with two variable parameters, equation 6-23, with Ruedenberg integral values.

Here it is interesting to note that, as expected,

$$\psi_{(1k_t+7)} = \psi_{(7k_t+1)},$$

for the same variable parameter k, if $k_t = 1/k_t$.

The energy obtained, the lowest for the benzyl radical was:-

-309.7805 e.V. $\qquad k = 5.1, \quad k_t = 0.325$

The resulting spin densities were:-

atom.no.	1	2	3	4	7
	-0.251	0.472	-0.281	0.472	0.457

As can be seen the spin densities have been considerably reduced - all values are less than 0.5. However, there is still insufficient density on the seventh atom, compared to the other atoms; in fact the density on the seventh atom is now less than that on the second and fourth atoms.

It seems, thus, an inherent feature of the NPSO method, as with the AMO wavefunction, that, although good energies can be obtained, reminimisation may be necessary for other physical properties.

vi) Further applications of the fully spin projected NPSO method.

Excited States of Azulene:

The spectra of alternant hydrocarbon molecules can be predicted relatively easily, in good agreement with experimental results. The theory of the spectra of alternant hydrocarbons is well documented,(136),(137). Because of the lack of pairing between occupied and unoccupied orbitals for non-alternant molecules, their spectra are not as easy to predict. Several attempts have been made,(133),(134). Here, using the fully spin projected NPSO method, attempts were made to predict azulene transitions.

Experimentally the following transitions have been observed:-

S_o- S_1 fluorescence at $\sim$ 13,200 cm^{-1},($_{131}$)

S_o- T_1 phosphorescence at $\sim$ 8,400 cm^{-1},($_{131}$).

The S_o- T_1 transition has also been reported at $\sim$ 11,600 cm^{-1}, (132); and this clash of observation lead Birks,(131), to say: " Reliable data on the lower excited states of azulene remains elusive."

Calculations:

The transition energies were calculated from the difference between the ground state - ^1A state - energy and the energies of the excited states - ^1B, ^3A, ^3B.

Calculations for the ground state have been previously reported, in this chapter. The ground state energy was taken as E = -496.43524 e.V., at k = 0.284.

Throughout these calculations the unprojected NPSO wavefunction was used to set up the first order density matrix

from which the natural orbitals were calculated.

For the ground state,

$$\Psi_T = \Psi_I + \Psi_{II} \qquad ..8\text{-}49$$

where

$$\Psi_I = A|(\chi_1+k\chi_2)(1)\alpha(1)\ (\chi_3+k\chi_4)(2)\alpha(2)\ (\chi_5+k\chi_6)(3)\alpha(3)\ (\chi_7+k\chi_8)(4)\alpha(4)\ (\chi_9+k\chi_{10})(5)\alpha(5)\ (\chi_2+k\chi_3)(6)\beta(6)\ (\chi_4+k\chi_5)(7)\beta(7)\ (\chi_6+k\chi_7)(8)\beta(8)\ (\chi_8+k\chi_9)(9)\beta(9)\ (\chi_{10}+k\chi_1)(10)\beta(10)| \qquad ..8\text{-}50$$

and Ψ_{II} was derived from Ψ_I by the application of the correct symmetry projection operator for the ^1A state,

$$\Psi_{II} = A|(k\chi_1+\chi_2)(1)\alpha(1)\ (\chi_4+k\chi_3)(2)\alpha(2)\ (\chi_6+k\chi_5)(3)\alpha(3)\ (\chi_8+k\chi_7)(4)\alpha(4)\ (\chi_{10}+k\chi_9)(5)\alpha(5)\ (\chi_2+k\chi_3)(6)\beta(6)\ (\chi_5+k\chi_4)(7)\beta(7)\ (\chi_7+k\chi_6)(8)\beta(8)\ (\chi_9+k\chi_8)(9)\beta(9)\ (\chi_1+k\chi_{10})(10)\beta(10)| \qquad ..8\text{-}51$$

For the excited states Ψ_T was derived from Ψ_I by the application of the appropriate symmetry projection operator for the state.

For the ^3A state,

$\Psi_T = \Psi_I + \Psi_{II}$, as previously; but for both the ^3B and ^1B states,

$$\Psi_T = \Psi_I - \Psi_{II} \qquad ..8\text{-}52$$

where Ψ_I and Ψ_{II} were previously defined, equations 8-50 and 8-51.

For the triplet states, spin projection will give different coefficients, C_k , in the Pauncz energy formula, equations 3-41 and3-46.

The values of the coefficients, when s = 1, (triplet) must be re-calculated from

$$C_k^{2s+1} = \frac{(-1)^k \cdot 3}{(n+1)(n+2)} \binom{n}{k}^{-1} (n-2k)$$

..8-53

Thus, by slight modification of the original density matrix NPSO program, it was possible to calculate the energies of the excited states. Ruedenberg integral values were used, with the Mulliken approximation. The minimum energy results are given in table VIII-13. Notice that both the B symmetry states have k almost equal, as do both the A states.

The calculated transition energies, with those of previous workers, and the experimental ones, are given in table VIII-14, in e.V.

It can be seen that our results compare favourably with those of Amos,(138), but not with those of Pariser,(133). Our calculations do not agree with the experimentally (135) obtained results. Since 1 e.V. = 8068 cm^{-1} these calculations give the transitions as:-

$S_o - S_1$	300 cm^{-1}
$S_o - T_1$	9128 cm^{-1}
$S_o - T_2$	9259 cm^{-1}

Since Pariser used semi-empirical data, and in general semi-empirical data gives good agreement with experimental results, we continued our calculations using the parametrization of Beveridge and Hinze,(139). The data used is given in table VIII-15. Nearest overlap

Results of the energy calculations for the various states of the azulene molecule.

all energies are given in e.V.

state	energy	k
^1A	-496.43524 e.V.	0.284
^1B	-496.39804 e.V.	0.312
^3A	-495.30377 e.V.	0.281
^3B	-495.28762 e.V.	0.3125

table VIII-13.

Calculated transition energies for azulene.

$S_o - S_1$	300 cm^{-1}
$S_o - T_1$	9128 cm^{-1}
$S_o - T_2$	9259 cm^{-1}

table VIII-14

Beveridge and Hinze data for azulene.

element	coulomb integral	overlap integral	Hamiltonian element
11	11.13	1.0	-24.76406
22			-24.73607
33			-31.42926
44			-24.75898
55			-24.75898
66			-24.77938
12	6.80203	0.24682	-3.55270
23	6.77404		-3.47341
34	6.80969		-3.57452
45	6.78929		-3.51652
39	6.68554		-3.22863

table VIII-15.

Results of the energy calculations for the various states of the azulene molecule, using Beveridge and Hinze data.

state	energy	k
^1A	-187.37069 e.V.	0.179
^1B	-187.37121 e.V.	0.185
^3A	-187.47765 e.V.	0.1875
^3B	-187.47516 e.V.	0.19

table VIII-16.

integrals were used,only, and the original integral values, not those suggested by Beveridge and Hinze, were used. Only coulomb integrals between nearest neighbours were used, since the Mulliken approximation would set these to zero, through the neglect of overlap.

The results as given in table VIII-16, are very disappointing. The excited states appear to have energies lower than the ground state. But previous NPSO calculations using semi-empirical data have also been less successful than those using theoretical integrals - thus the results may reflect the inadequacy of trying to perform an NPSO calculation with semi-empirical data. Since calculations on the excited states of benzene (52) were quite successful, it seems that with further work, it should be possible to improve the results obtained here.

IX. CONCLUSION.

The correlation energy for a system may be considered as the difference between the exact solution of the non-relativistic Schrödinger wave equation and the HF energy; but the correlation considered in this thesis has been limited further. We have been calculating molecular wavefunctions and ground state energies using only the pi-electrons of the molecules. The energy contribution due to the sigma-electrons was assumed constant and independant of the pi-electron structure, and included in the hamiltonian term $h_{core}(i)$ were all the nuclear effects. Numerous other calculations have worked within the same restrictions.

Previous workers have shown the NPSO method to be a successful way of writing a molecular wavefunction which takes into account pi-electron correlation. Benzene has frequently been used as a test molecule; and for benzene the NPSO method gives good results.

Empedocles and Linnett,(52) made a thorough investigation of the NPSO method as applied to the benzene molecule, and compared their results with those obtained by different methods. From Moskowitz and Barnett's Molecular Orbital energy,(57), and their configuration interaction result,(with twenty one adjustable paramenters,) it is possible to estimate the correlation energy for benzene. The best NPSO energy showed that 97% of this correlation energy could be accounted for by this method, using only two adjustable parameters. (If the weightings of the two components of the total wavefunction, Ψ , a_1 and a_2 ,

where $\Psi = a_1\psi_1 + a_2\psi_2$, are assumed, the number of variable parameters reduces to one.) The comparable AMO wavefunction, with two variable parameters, (58), accounted for 90% of the correlation energy. Further simplification of the AMO and NPSO methods, such that only one adjustable constant, k, for the NPSO method, is used, produces, as expected, a lowering in the amount of correlation energy included in the ground state energy. The one-parameter AMO, (129), includes about 78% of the correlation energy, whereas the comparable NPSO method accounts for about 91%. Thus the NPSO method, using one adjustable parameter is marginally better than the two-parameter AMO method. Ebbing and Poplawski, (59), applied the separated-pair, or geminal theory, (130) to benzene. The lowest ground state energy obtained by them, including an allowance for resonance, contained only 64% of the correlation energy. Hence for the benzene molecule, the NPSO method is superior.

Pauncz (85) said of the NPSO method, that it surpasses the AMO method for small molecules, but he questioned the feasibility of the calculations being extended to larger systems. The results in this thesis for azulene, phenanthrene, anthracene and the benzyl radical show that the calculations are possible. The problem of non-orthogonality is surmountable, by ignoring cross terms between determinants, and using the method of King et al. (70), for forming orthogonal one-electron orbitals. It is thus possible to obtain an NPSO energy, unprojected, using a one adjustable parameter wavefunction which is better than that obtained from a five-parameter

AMO method, for azulene. Optimising the anti-bonding starting orbitals for the five-parameter AMO method lowers the energy below the unprojected NPSO result; but the annihilated NPSO energy, (where some account was made for spin projection) gives a better energy than even this AMO result.The inclusion of full spin projection into the NPSO wavefunction lowers the energy even further.

For all three large hydrocarbon molecules studied, azulene, anthracene and phenanthrene, the unprojected NPSO wavefunction with one adjustable parameter gives a lower ground state energy than the comparable AMO method. The inclusion of some spin projection lowers the energy even further. So it seems that for large hydrocarbon molecules the NPSO method makes good allowance for electron correlation. "If a major portion of correlation energy can be obtained for a large class of molecules the method may be deemed successful."(59).

One further point in favour of the NPSO method: for conjugated hydrocarbon molecules the assumption that the adjustable parameter, k, is 0.25 is not too drastic. Hence a wavefunction which has intuitive meaning, in terms of lone pairs, bonds and inner shells can be quickly written for hydrocarbon molecules.

The spin density calculations for radicals and ions were less successful than the energy calculations. Several reasons have already been suggested for the poor results for the benzyl radical. One further suggestion is made here. Vincow and Johnson,(92) obtained good hyperfine coupling constants using the AMO method, but they obtained the wavefunction used in their calculations by criteria other than minimum ground state energy. Other workers

have considered the criteria for good wavefunctions,(111), and found it necessary to reminimise the wavefunction to obtain satisfactory charge distributions,(112). Perhaps, as with the AMO method, the spin densities should be calculated from the "best" NPSO wavefunction found by criteria other than minimum energy.

The preliminary calculations on the excited states of azulene were not as good as hoped, but further work may improve them.

For the three large hydrocarbon molecules studied in this work, and the benzyl radical, the best NPSO ground state energy is calculated by the fully spin projected method. This is, as expected, since the wavefunction formed by such a method is an eigenfunction of the spin operators, and so satisfies the criteria for a good wavefunction. This fully spin projected method used the first order density matrix formed from a symmetry projected NPSO wavefunction, and through the use of natural orbitals forms a single determinantal wavefunction. The wavefunction has pairing properties similar to those of an AMO wavefunction, and so the fully spin projected energy can be calculated.Using this NPSO method it should be possible to perform NPSO calculations to include the bridge bond explicitly, by using a wavefunction of the form

$$\Psi_T = a_1 \Psi_1 + a_2 \Psi_2$$

where Ψ_1 , as previously used, spans the external bonds, and Ψ_2 includes the bridge bond.

The spin density results for the benzyl radical are improved by this method, and perhaps here is where more work should be done.

In conclusion, although lack of orthogonality of the initial semi-localised orbitals formed in the NPSO method makes computation, using the wavefunction difficult, it is possible, using either approximate methods, or a synthesis of both DODS methods,(AMO and NPSO), to calculate good ground state energies, even for large hydrocarbon molecules.

Appendix I.

Integral approximations, after Ruedenberg,(82).

Hamiltonian elements over atomic orbitals.

All Hamiltonian matrix elements were calculated within the "tight - binding formulation" of Ruedenberg.

$$H_{pq} = \langle \chi_p | -\frac{\hbar^2}{2m}\nabla + \sum_r U_r^c + \sum_n U_n^H | \chi_q \rangle$$

where U_i^H denotes the potential energy of an electron in the field of a hydrogen atom,
and U_p^c denotes the potential energy of an electron in the field of a carbon atom.

The diagonal elements reduce to

$$H_{pp} = \langle \chi_1 | -\frac{\hbar^2}{2m}\nabla | \chi_1 \rangle + U_{pp} + \sum_{i=1}^{n} (ii|pp)$$

where U_{pp} is the sum of the various penetration integrals, depending on the position of the carbon atom.
For a joint atom, P,

$$U_{pp} = \langle \chi_1 | U_1^c | \chi_1 \rangle + 3\langle \chi_1 | U_2^c | \chi_1 \rangle \quad ;$$

for a non-joint carbon atom, P,

$$U_{pp} = \langle \chi_1 | U_1^c | \chi_1 \rangle + 2\langle \chi_1 | U_2^c | \chi_1 \rangle + \langle \chi_1 | U_n^H | \chi_1 \rangle \quad ;$$

and

$$U_{pp} = \langle \chi_1 | U_1^c | \chi_1 \rangle + \langle \chi_1 | U_2^c | \chi_1 \rangle + 2\langle \chi_1 | U_n^H | \chi_1 \rangle$$

if P is at the end of a conjugated hydrocarbon chain.

$(ii|pp)$ is a coulomb integral between atoms i and p.

The integrals $\langle \chi_1 | U_1^c | \chi_1 \rangle$ and $\langle \chi_1 | U_2^c | \chi_1 \rangle$ are carbon penetration integrals calculated using the formula given in equation 5.2 and 3.10 in reference 82, page 1895. The numerical values, quoted in e.V., not as in Ruedenberg's work, depend on internuclear distance, except for:-

$$\langle \chi_1 | U_1^c | \chi_1 \rangle = 36.296897 \text{ e.V.}$$

The integral $\langle \chi_1 | U_H^H | \chi_1 \rangle$ is a hydrogen penetration integral calculated by equations 6.7, 6.8, and 6.9, page 1896, reference 82 ; its numerical value is 0.610669 e.V.

The off-diagonal elements of the Hamiltonian were calculated from

$$H_{pq} = \beta_{pq} - \sum_j (pq|jj)$$

where

$$\beta_{pq} = \langle \chi_p | \left(-\frac{h^2}{2m}\nabla\right) | \chi_q \rangle - 2\langle \chi_p | U_1^c | \chi_q \rangle$$

The carbon penetration integrals $\langle \chi_p | U_1^c | \chi_q \rangle$ were again calculated using Ruedenberg's method, equation 4.4, page 1895, reference 82 .

Using Mulliken's approximation, (83), that

$$\langle pq|rs\rangle = \tfrac{1}{4} S_{pq}\delta_{rs}\{\langle pp|rr\rangle + \langle qq|rr\rangle + \langle pp|ss\rangle + \langle qq|ss\rangle\}$$

where S_{pq} is an overlap integral between the atomic orbitals χ_p and χ_q ,

and $\langle qq|rr\rangle$ is a coulomb integral,

the off-diagonal elements of the Hamiltonian reduce to:-

$$H_{pq} = \beta_{pq} - \sum_j \tfrac{1}{2} S_{pq} \{ \langle pp|jj\rangle + \langle qq|jj\rangle \}$$

Overlap integrals.

All overlap integrals were calculated exactly, but using the orbital exponent suggested by Ruedenberg; viz:-

ζ (orbital exponent) = 1.161789.

Coulomb integrals.

$$\langle pq|rs\rangle = \iint \chi_p(1)\, \chi_q(1)\, \frac{1}{r_{12}}\, \chi_r(2)\, \chi_s(2)\, \delta\tau_1\, \delta\tau_2$$

One and two centre coulomb integrals were calculated using Roothaan's method,(126).

All other multi-centred two electron integrals were calculated using the Mulliken approximation.

$$\langle pq|rs\rangle = \tfrac{1}{4} S_{pq}\, S_{rs} \{ \langle pp|rr\rangle + \langle qq|rr\rangle + \langle pp|ss\rangle + \langle qq|ss\rangle \}$$

Kinetic energy integrals.

$\langle \chi_1 | -\frac{\hbar^2}{2m} \nabla | \chi_1 \rangle$, the kinetic energy integrals were also calculated per Roothaan.

$$\langle \chi_{2p\pi a} | -\frac{\hbar^2}{2m}\nabla | \chi_{2p\pi b} \rangle = \frac{1}{2}\zeta^2(1+\tau^2)$$
$$\left\{ (2p\pi_a | 2p\pi b) - \frac{4}{\sqrt{3}} (1p\pi a | 2p\pi b) \right\}$$

where

ζ = orbital exponent = 1.161789

$\tau = (\zeta_a - \zeta_b)/(\zeta_a + \zeta_b)$, which for two orbitals of the same exponent, is zero.

$$(2p\pi_a | 2p\pi b) = \left[1 + \rho + \frac{2}{5}\rho^2 + \frac{1}{15}\rho^3\right] e^{-\rho}$$

(equation 2.1, reference 82, p.1893.)

and

$$(1p_\pi | 2p\pi b) = \frac{\sqrt{3}}{2}\left[1 + \rho + \frac{1}{3}\rho^2\right] e^{-\rho}$$

where R = interatomic distance,

and

$$\rho = \frac{1}{2}(\zeta_a + \zeta_b) \times R.$$

Appendix II.

Integral approximations, after Goeppert-Mayer and Sklar,(97).

Hamiltonian elements over atomic orbitals.

The Goeppert-Mayer Sklar core integrals differ from those calculated by Ruedenberg's method in that the hydrogen atoms and their effects are neglected, and the potential due to a carbon nucleus is set to the potential of a neutral carbon atom in the valence state, minus the charge distribution of an electron in a pi- orbital, ie. U_p^+ .

Thus the elements are given by

$$H_{pq} = \langle \chi_p | -\frac{\hbar^2}{2m}\nabla + \sum_r U_r^+ | \chi_q \rangle$$

The diagonal elements reduce to

$$H_{pp} = \langle \chi_p | -\frac{\hbar^2}{2m}\nabla | \chi_p \rangle + U_p^+ + \sum_{q \neq p} U_q^+ .$$

But $\langle \chi_p | -\frac{\hbar^2}{2m}\nabla | \chi_p \rangle + U_p^+$

is equal in magnitude, to the ionisation potential of a carbon atom:

$$\therefore H_{pp} = -I_p + \sum_{q \neq p} U_q^+ .$$

The potential of the carbon nucleus is equal to the potential of a neutral carbon atom, U_p^o , minus a penetration integral, $(p|\,qq)$.

Thus

$$H_{pp} = -I_p - \sum_{q \neq p} (pp|qq) - \sum_{q \neq p} (p|qq)$$

I_p was set equal to 11.22 e.V., Ruedenberg's value,(82). The penetration integrals were calculated by Ruedenberg's method, (equation 4-4, reference 82,p.1895), as previously.

The off-diagonal elements were calculated as previously,

$$H_{pq} = \beta_{pq} - \sum_j (pq|jj)$$

Which reduces, (through the use of the Mulliken approximation,) to

$$H_{pq} = \langle \chi_p | -\frac{\hbar^2}{2m} \nabla | \chi_q \rangle - 2\langle p|qq\rangle - \frac{1}{2}\sum_j S_{pq} (\langle pp|jj\rangle + \langle qq|jj\rangle)$$

Coulomb integrals.

The coulomb integrals were calculated as previously, except that for the calculation of the Hamiltonian matrix elements, the one-centre integral was calculated from the relationship:

$$I_p = A_r + (11|11)$$

Overlap integrals.

As previously complete overlap was included. All integrals were calculated as previously.

References.

1 Schrödinger, E., Ann. Physik, 79,(1926),361,489,734; Ann. Physik, 81,(1926),109; Phys.Rev., 28, (1926),1049.

2 Born, M., and Oppenheimer, J.R., Ann. Physik, 84,(1927),451

3 Hartree, D.R., Proc. Camb. Phil. Soc., 24,(1928),84,111.

4 Pilar,F.L., Elementary Quantum Chemistry,(1968), McGraw-Hill,(New York), p.176.

5 Löwdin, P.O., Adv. Chem. Phys., 2.(1959),207.

6 Wigner,E.P., and Seitz,F., Phys. Rev., 43,(1933),304; Phys. Rev., 46,(1934),509.
Slater,J.C., Phys. Rev., 81,(1951),385.

7 Pauli,W., Z. Physik, 31,(1925),765.

8 reference 5, p.216.

9 Slater,J.C., Phys. Rev., 34,(1929),1293.

10 Fock,V., Z. Physik, 61,(1930),126; 62,(1930),795.

11 reference 4, p.488f.

12 Sinanoglu,O., J. Chem. Phys., 33,(1960),1212; 36,(1962), 706,3198; Phys. Rev., 122,(1961),493; Proc. Roy. Soc.(London), A260,(1961),379.

13 Kolos,W., and Roothaan,C.C.J., Rev. Mod. Phys., 37, (1962),193.

14 Hylleraas,E.A., Z. Physik, 65,(1930), 209.

15 James,H.M., and Coolidge,A.S., J. Chem. Phys. 32, (1960), 219.

16 Szasz,L., Phys. Rev., 126,(1962),169; J. Chem. Phys. 37,(1962),193.

17 Craig,D.P., Proc. Roy. Soc.(London), A200,(1950),474.

18 Hylleraas,E.A., Z. Physik, 48,(1928),469.

19 Löwdin,P.O., Phys. Rev., 97,(1955),1474.

20 Slater,J.C., Phys. Rev., 35,(1930),210.

21 Gilbert,T.L., J. Chem. Phys., 43,(1965),s248

22 reference 5, p. 307.

23 reference 5, p.235.

24 Courant,R., differential and Integral Calculus, vol.II, Blackie and Son,(London),(1936), p.190.

25 Hartree,D.R., The Calculation of Atomic Structures, John Wiley and Sons,(New York),(1957),p.22.

26 Roothaan,C.C.J., Rev. Mod. Phys., 23,(1951),69.

27 Coulson,C.A., Proc. Roy. Soc.,(London), A169,(1939),413.

28 Roothaan,C.C.J., Rev. Mod. Phys., 32,(1960), 179.

29 Davidson,S.G., Physical Chemistry, An Advanced Treatise, III, p.98, (1969), Academic Press(New York).

30 reference 5, p.227f.

31 Huzinaga,S., Phys. Rev.,120,(1960),866.

32 Pauncz,R., Physical Chemistry, An Advanced Treatise, III, p.185, (1969), Academic Press (New York).

33 Nesbet,R.K., Proc. Roy. Soc.(London), A230,(1955),312.

34 Pople,J.A., and Nesbet,R.K., J. Chem. Phys., 22,(1954),571,

35 Segal,G.A., J. Chem. Phys., 52,(1970),3530.

36 Löwdin,P.O., Rev. Mod. Phys., 32,(1960), 328; 36,(1964),966.

37 Hall,G.G, and Amos,A.T., Adv. Atom.and Mol. Structure,I, (1965),p.12, Academic Press,(new York).

38 Goddard,W.A., Phys. Rev., 157, (1967),73,81,93.

39 Marshall,W., Proc. Phys. Soc., A78,(1961),113.

40 Amos,A.T., and Hall,G.G., Proc. Roy. Soc.,(London),A263, (1961),483.

41 Amos,A.T., and Snyder,L.C., J. Chem. Phys., 41,(1964),1773.

42 Snyder,L.C., and Amos,A.T., J. Chem. Phys., 42,(1965),3670.

43 Claxton,T.A. and McWilliams,D., Theoret. chim. Acta, 16, (1970), 346.

44 Amos,A.T., Mol. Phys., 5,(1962),91.

45 Parr,R.G., Quantum Mechanics of Molecular Electronic Structure. W.A.Benjamin,(New York),(1964).

46 Lykos,P.G., and Parr,R.G., J. Chem. Phys., 24,(1956),1166.

47 Nakatsuji,H., Kato,H., and Yonezawa,T., J. Chem. Phys., 51, (1969), 3175.

48 Sasaki,F., and Ohno,K., J. Math. Phys., 4,(1963), 1140.

49 Linnett,J.W., J. Am. Chem. Soc., 83,(1961), 2643.

50 Slater,J.C., Phys. Rev. 37,(1931), 481; 38,(1931),1109.
Pauling,L., J. Am. Chem. Soc., 53,(1931), 1367,3225; 54, (1932),998, 3570.
Heitler,W., and London,F., Z. Physik, 44,(1927),455.

51 Hirst,D.M., and Linnett,J.W., J.Chem. Soc.,(London), (1962), 1035,3844.

52 Empedocles,P.B., and Linnett,J.W., Proc. Roy. Soc.,(London) A282,(1964),166.

53 Hirst,D.M., and Linnett,J.W., J. Chem. Phys., 43,(1965),s74

54 Hirst.D.M.,and Linington,M.E., Theoret. chim. Acta, 22,(1971), 315.

55 Lewis,G.N., J. Am. Chem. Soc.,38, (1916),762.

56 Linnett,J.W., The Electronic Structure of Molecules, A New Approach. Methuen,(London) Ltd.(1964).

57 Moskowitz,J.W., and Barnett,M.P., J. Chem. Phys., 18, (1950), 1561.

58 de Heer,J., J. Phys. Chem., 66, (1962), 2288.

59 Ebbing,D.D., and Poplawski,L.E., J. Chem. Phys. 45,(1966), 2657.

60 Mueller,C.R., and Eyring,H., J. Chem. Phys.,19,(1951), 1495,1498.

61 Coulson,C.A., and Fischer,I., Phil. Mag.,40,(1949),386.

62 Hopton,J.D., and Linnett,J.W., J. Chem. Soc.,(London), (1962),1553.

63 Wigner,E.P., Group Theory, (1959), Academic Press,(New York

64 Amos,A.T., and Hall,G.G., Proc. Roy. Soc.,(London), A263, (1961),483.

65 Löwdin,P.O., J. Appl. Phys. Suppl., 33, (1962),251.

66 Dirac,P.A.M., The Principles of Quantum Mechanics,(1930).

67 Pauncz,R., Alternant Molecular Orbital Method, (1967), W.B.Saunders Company,

68 Harris,F.E., Adv. in Qu. Chem., 3,(1967),61.

69 Gerratt,J., and Lipscomb,W.N., Proc. Nat. Acad. Sci. 59,(1968), 323.

Gerratt,J., Adv. At. Mol. Phys. 7, (1972)

70 King,F.H., Stanton,R.E., Kim,H., Wyatt,R.E., Parr,R.G., J. Chem. Phys., 47,(1967),1936.

71 Pauncz,R., Silberman,Z., and Gershgorn,Z., Int. J. Qu. Chem. 2, (1968),453.

72 Slater,J.C., Phys.Rev. 81,(1951),385.

73 Salem,L., The Molecular Orbital Theory of Conjugated Systems. (1966), Benjamin,(New York).

74 reference 67, p.152.

75 Silberman,Z., and Pauncz,R., Theoret. chim. Acta., 10,(1968),254.

76 Empedocles,P.B., and Linnett,J.W., Theoret. chim. Acta., 4,(1966),377.

77 Duke,B.J., Theoret. chim. Acta, 8,(1967),87.

78 Hirst,D.M. and Mackey,P.H., Chem. Phys. Letts.,3,(1969),255
Hirst,D.M. and Linington,M.E., Theoret. chim. Acta, 22,(1971),315.

79 Parker,G.W. and Memory,J.D., Bull. Am. Phys. Soc., 9, (1964),102.

80 Cruickshanks,D.W.J. and Sparks,R.A., Proc. Roy. Soc., (London),A258, (1960),270.

81 Trotter,J., Acta Crys., 16,(1963),606.

82 Ruedenberg,K., J. Chem. Phys.,34,(1961),1861,1878,1892,1907

83 Mulliken,R.S., J. Chim. Phys.,46,(1949),497,675.

84 Hirst,D.M. and Linington,M.E., J. Chem. Soc.,(London), Farad. Trans.II, 68,(1972),1988.

85 reference 67, p.212.

86 Fischer,H., Z. Naturforsch, 20, (1965), 488.

87 Carrington,A. and Smith,I.C.P., Mol. Phys.,9,(1965),138; and referneces therein.

88 Ramondi,M., Simonetta,M. and Tanardini,G.F., J. Chem. Phys. 56,(1972),5091.

89 Harriman,J.E. and Sando,K.M., J. Chem. Phys.,48,(1968),5138.

90 Kruglyak,Y.A. and Ukrainsky,I.I., Int.J. Quan. Chem. 4,(1970),57.

91 Shanshal,M., Mol. Phys.,23,(1972),441.

92 Vincow,G. and Johnson,P.M., J. Chem. Phys.,39,(1963),1143.

93 Devaux,P., J. Chem. Phys.,52,(1970),6436.

94 Pariser,R. and Parr,R.G., J. Chem. Phys.,21,(1953),466,767.

95 Bloor,J.E. and Gilson,B.R., QCPE 77.1, Indiana University, Bloomington, Indiana, U.S.A.

96 Amos,A.T. and Burrows,B.L., J. Chem. Phys.,52,(1970),3072.

97 Goeppert-Mayer,M. and Sklar,A.L., J. Chem. Phys., 6,(1938),645.

98 Karplus,M. and Shavitt,I., J. Chem. Phys.,38,(1963),1256.

99 McConnell,H.M., J. Chem. Phys.,28,(1958),1188.

100 Dearman,H.H. and McConnell,H.M., J. Chem. Phys., 33, (1960),1877.

101 Berthier,G. and Baudet,J., J. Chim. Phys.,60,(1963),1161.

102 Streitwieser,A.J., Molecular Orbital Theory for Organic Chemists, Wiley,New York.,(1961).

103 Harris,F.E., Mol. Phys., 11,(1966),243.

104 Colpa,J.P. and Bolton,J.R., Mol. Phys., 6,(1963),273.

105 Giacometti,G., Nordio,P.L. and Pavan,M.V., Theoret. chim. Acta, 1,(1963), 404.

106 Benson,H.G. and Hudson,A., Mol. Phys., 20,(1970),185.

107 Beveridge,D.L. and Guth,E., J. Chem. Phys.,55,(1970),458.

108 Hirst,D.M. and Linnett,J.W., J. Chem. Soc.,(London), (1963),1068.

109 Hansen,A.E., Theoret. chim. Acta,7,(1967),230.

110 reference 67, p.187.

111 Kutzelnigg,W. and Smith,V.H., J. Chem. Phys., 41, (1964), 896.

112 Hoyland,J.R. and Goodman,L., J. Chem. Phys.,34,(1961),1446.

113 Amos,T. and Woodward,M., J. Chem. Phys.50,(1969),119.

114 Hinchliffe,A., J. Mol. Str.,10,(1971),379.

115 Kato,H., Konishi,H., Yamabe,H., Yonezaw,T., Bull. Chem. Soc. Japan, 40,(1967),1262.

Longuet-Higgins,H.C. and Murrell,J.N., Proc. Phys. Soc., A68,(1955),601.

116 Löwdin,P.O., Phys. Rev.,97,(1955),1474.

117 Claxton,T.A. and Weiner,B., Trans. Fad. Soc.,66,(1970),2113.

118 McWeeny,R. and Sutcliffe,B.T., Methods of Molecular Quantum Mechanics, (1969),Academic Press.

119 Von Neumann,J.,Mathematische Grundlagen der Quantenmechanick. Springer , Berlin,(1932).

120 McWeeny,R., Spins in Chemistry,(1970), Academic Press.

121 Harriman,J.E., Int. J. Qu. Chem., Proc. Int. Symposium on At. Mol. and Solid State Theory, and Qu. Biol. 4,(1971),363.

122 Löwdin,P.O., Phys. Rev., 97,(1955),1490.

123 Kutzelnigg,W., Z. Naturforsch, 18,(1963),1058;20,(1965), 168.

124 Davidson,E.R. and Bender,C.F., J. Chem. Phys.,47,(1967),360 J.Phys . Chem.,70,(1966),2675.

125 McWeeny,R. and Kutzelnigg,W., Int. J. Qu. Chem.,II,(1968), 1807.

126 Roothaan,C.C.J. J. Chem. Phys.,19,(1951),1445.

127 Löwdin,P.O., Adv. Chem. Phys.,14,(1970),283.

128 Sinanoğlu,O., Adv. Chem. Phys.,14,(1970),237.

129 Nesbet,R.K., Adv. Chem. Phys.,9,(1965),321.

130 Paunez,R., J. Chem. Phys.,37,(1962),2739.

131 Birks,J.B. The Photophysics of Aromatic Molecules, p.627, Wiley,(1972).

132 Rentzepis,P.M., Chem. Phys. Letts.,3,(1969),717.

133 Pariser,R., J. Chem. Phys.,25,(1965),1112.

134 Koutecký,J., Hochman,P. and Michl,J.,J. Chem. Phys., 40,(1964),2439.

135 Mann,D.E., Platt,J.R. and Klevens,H.B., J. Chem. Phys., 17,(1949),481.

136 Murrell,J.N., The Theory of the Spectra of Organic Molecules,(1963), London.

137 Peacock,T.E., Electronic Properties of Aromatic and Heterocyclic Molecules,(1965), Academic Press.

138 Amos,A.T., Mol. Phys.,5,(1962),91.

139 Beveridge,D.L. and Hinze,J.,J.A.C.S.,93,(1971),3107.

140 Reference 67, p.163.

141 Löwdin,P.O., Arkiv. Math. Astro. Fys.,(1948),35A.

142 Harriman,J.E., J. Chem. Phys.,40,(1964),2827.

143 Koutecký,J., J. Chem. Phys.,45,(1966),3668.